A study on mechanical properties, electrical conductivity and EMI shielding performance of syntactic foams.

Zhang, Liying.

2013

Zhang, L. (2013). A study on mechanical properties, electrical conductivity and EMI shielding performance of syntactic foams. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/53735>

<https://doi.org/10.32657/10356/53735>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**A STUDY ON MECHANICAL PROPERTIES, ELECTRICAL
CONDUCTIVITY AND EMI SHIELDING PERFORMANCE
OF SYNTACTIC FOAMS**

ZHANG LIYING

School of Materials Science and Engineering

2013

**A STUDY ON MECHANICAL PROPERTIES, ELECTRICAL
CONDUCTIVITY AND EMI SHIELDING PERFORMANCE
OF SYNTACTIC FOAMS**

ZHANG LIYING

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2013

Acknowledgement

I would like to extend my gratitude to a number of people for their kindly support and assistance during the course of this work.

Firstly, I would like to give sincere acknowledgements to my supervisor, Prof. Ma Jan, for his continuous valuable guidance, encouragement and support for my project. His critical advices keep me in the right direction for the research. I would also like to express my deeply appreciation to my co-supervisor Prof. Lu Xuehong, for her guidance and fruitful discussions. Thanks are also extended to Prof Kong Linbing, Prof. Fong Wen Mei Eileen, Prof See Kye Yak, and Prof Chen Lang for their kind assistance. A special thank you goes to Mr. Wang Lin Biao for his assistance with the EMI shielding measurements and paper revision. Thanks also give to Dr. Goh Chin Foo, Dr. Cheng Hao, Dr Liu Ming, Dr. Xiong Shanxin, Dr Du Zehui, Dr. Yang Kai, Dr. Sun Ting, Dr. Lu Jie for sharing the experiences and suggestions.

Secondly, I am sincerely grateful to all technicians in MSE, especially Mr. Tan Yong Kwang and Mrs. Tay Poh Tin, for equipment training.

Finally, I have no words to express my gratefulness to my parents. Thank you for everything. The greatest thanks also give to my wife, Chen Min, for her caring and support during the last 4 years and throughout my entire time in MSE. I am also grateful to all my friends for their emotional support and encouragement.

Abstract

Syntactic foam is a special class of light weight composite materials. It has been found useful in many areas, such as aerospace and submarine. In order to further widen its application spectrum, the enhancement in the mechanical properties of syntactic foams is essential. Besides mechanical properties, their electromagnetic interference (EMI) shielding has not been explored because of the non-conductive nature of the traditional fillers and matrices of syntactic foams. However, due to their light weight advantage, syntactic foams become an attractive candidate for EMI shielding applications, for electronic devices and electrical equipments. Therefore, developing syntactic foams with good mechanical properties and/or EMI shielding performance would expand their applications for future composite materials.

In this work, hollow carbon microspheres (HCMs), instead of the traditional non-conductive microspheres, were employed to fabricate syntactic foams with phenolic resin as matrix. In the attempts to improve mechanical properties and/or EMI shielding performance of the resultant foams, three different approaches, namely coupling agent, carbonization and carbon nanofiber (CNF) reinforcement, were applied.

In the first approach, the effect of coupling agent on mechanical properties and EMI shielding performance of syntactic foams was studied. Results showed that better interfacial adhesion could be induced from the coupling agent treated HCMs, which led to the enhancement in compressive strength, flexural strength and fracture toughness of the syntactic foams. Toughness mechanisms, including crack deflection, crack bowing and debonding, were proposed. However, EMI testing results showed that the introduction of coupling agent had no effect on the EMI shielding performance, because a three-dimensional electrically conductive network was not formed.

In the second approach, the effect of carbonization on mechanical properties and EMI shielding performance of the syntactic foams was studied. The electrical conductivity was increased by approximately seven orders of magnitude, which resulted in a significant enhancement in shielding effectiveness (SE) by a factor of 16. The SE of 30 dB meant a shielding of over 99.9% of incident electromagnetic (EM) radiation. The shielding mechanisms were discussed in detail. However, it was also found that compressive and flexural strengths of the foams decreased due to the formation of glassy carbon and oversized internal voids after fully carbonization.

The third approach encompassed the inclusion CNFs. Results showed that no enhancement in compressive strength with the addition of CNFs was observed. Flexural strength and fracture toughness were increased with increasing CNFs content and decreased beyond 1.5 vol% of CNFs. The decreasing trend was due to agglomeration and clustering of the CNFs. Toughening mechanisms, such as crack deflection, step structure and debonding of the CNFs, were proposed. It was also found SE of the CNF reinforcement syntactic foams (CNFRSFs) was increased with increasing CNFs content and was superior to those of the composites having either CNFs or HCMs only. SE of 25 dB was achieved in the syntactic foam having 2.0 vol% CNFs, which is good enough for most practical applications. The shielding mechanisms were discussed in detail.

Table of Contents

Acknowledgement.....	i
Abstract.....	ii
Table of Contents	iv
List of Figures.....	viii
List of Tables.....	xii
List of Abbreviations	xii
Chapter 1. Introduction.....	1
1.1 Background	1
1.2 Problem statement, hypothesis and objectives	4
1.3 Scope	5
Chapter 2. Literature review	8
2.1 Introduction of syntactic foam	8
2.2 Materials used in syntactic foam	10
2.2.1 Binder	10
2.2.2 Filler	20
2.3 Preparation methods of syntactic foam	26
2.4 Mechanical behavior of syntactic foam.....	29
2.4.1 Compressive properties	29
2.4.2 Flexural properties.....	31
2.4.3 Fracture toughness.....	32
2.5 Factors affecting the mechanical properties of syntactic foam	33
2.5.1 Volume fraction of microspheres	33
2.5.2 Matrix/microspheres adhesion	35
2.5.3 Fiber reinforcement effect	36

2.6 Summary of mechanical properties of syntactic foam	38
2.7 EMI SE of polymer composites	40
2.7.1 EMI shielding theory and mechanism.....	40
2.7.2 SE model for composites.....	44
2.7.3 Polymer composites for shielding.....	45
2.8 Approaches on improving the SE performance	46
2.8.1 Dispersion of conductive filler.....	46
2.8.2 Carbon matrix.....	47
2.8.3 Nanofiber reinforcement effect	48
2.9 Summary	49
Chapter 3. Effect of coupling agent on mechanical properties and EMI shielding	
 performance of syntactic foams.....	51
3.1 Introduction	51
3.2. Materials and experimental procedures.....	52
3.2.1 Raw materials.....	52
3.2.2 HCM surface treatment	52
3.2.3 Preparation of syntactic foam.....	52
3.2.4 Fourier transformed infrared (FTIR) spectrometer	53
3.2.5 Mechanical tests	53
3.2.6 SE measurements	54
3.3 Results and Discussion.....	55
3.3.1 FTIR spectroscopy	55
3.3.2 Effect of coupling agent on compressive properties	57
3.3.3 Effect of coupling agent on flexural properites.....	61
3.3.4 Effect of coupling agent on fracture toughness.....	66
3.3.5 Effect of coupling agent on SE.....	70

3.4 Concluding remarks	71
Chapter 4. Effect of carbonization on mechanical properties and EMI shielding performance of syntactic foams.....	73
4.1 Introduction	73
4.2 Materials and experimental procedures.....	74
4.2.1 Raw materials	74
4.2.2 Preparation of syntactic carbon foam.....	74
4.2.3 Mechanical and EMI SE measurements.....	75
4.2.4 Electrical conductivity measurements.....	76
4.2.5 Raman spectroscopy measurements.....	76
4.2.6 Microstructural characterization.....	76
4.3 Results and discussion.....	76
4.3.1 Shrinkage and weight loss.....	76
4.3.2 Microstructure of the syntactic carbon foam.....	78
4.3.3 Effects of temperature on electrical conductivity.....	79
4.3.4 Effect of carbonization on SE	81
4.3.5 Effects of temperature on compressive and flexural properties	84
4.4 Concluding remarks	87
Chapter 5. CNFs reinforcement on mechanical properties and EMI shielding performance of syntactic foams.....	88
5.1 Introduction	88
5.2 Materials and experimental procedures.....	88
5.2.1 Raw materials	88
5.2.2 Preparation of carbon nanofiber reinforcement syntactic foams (CNFRSFs).....	89
5.2.3 Preparation of CNF composites	89

5.2.4 Mechanical and EMI SE tests	90
5.2.5 Electrical conductivity measurements	90
5.2.6 Microstructural characterization.....	90
5.3 Results and discussion.....	90
5.3.1 Effect of CNFs reinforcement on compressive property.....	90
5.3.2 Effect of CNFs reinforcement on flexural property	93
5.3.3 Effect of CNFs reinforcement on fracture toughness.....	96
5.3.4 Effect of CNFs reinforcement on SE	100
5.4 Concluding remarks	105
Chapter 6. Conclusions and future work.....	107
6.1 Conclusions	107
6.2 Future work	110
Reference.....	113
Publication List.....	131

List of Figures

Figure 1.1 Typical composite materials used in aircraft [1].	2
Figure 1.2 Project outline.	6
Figure 2.1 A representative sketch showing (a) two phase structure involving matrix and microspheres and (b) three phase structure in the presence of voids [23].	9
Figure 2.2 SEM image of syntactic foam.	10
Figure 2.3 Chemical structure of digycidyl ether of bisphenol-A.	12
Figure 2.4 Chemical structure of diamine.	12
Figure 2.5 Schematic process of chemical reaction between DGEBA and diamine.	12
Figure 2.6 Chemical structure of melamine phosphate (MP).	13
Figure 2.7 Chemical reaction of formaldehyde in aqueous solution	15
Figure 2.8 Schematic preparation process of novolac resin	16
Figure 2.9 Chemical structure of hexamethylenetetramine	16
Figure 2.10 Schematic preparation process of resol resin	18
Figure 2.11 Curing reaction of resole resin.	18
Figure 2.12 Preparation and curing processes of phenolic resin.	19
Figure 2.13 SEM image of hollow glass microspheres.	22
Figure 2.14 SEM image of hollow phenolic microspheres.	23
Figure 2.15 SEM image of hollow carbon microspheres	24
Figure 2.16 Compressive stress against engineering strain for syntactic foams.	30
Figure 2.17 Schematic representation of crack origination and propagation for specimens with (a) high aspect ratio and (b) low aspect ratio.	30
Figure 2.18 Flexural stress against engineering strain for syntactic foams.	32
Figure 2.19 SEM image of the fracture surface of short carbon fiber reinforced syntactic foam.	37

Figure 2.20 EM plane wave is normal incident to a material with thickness D.	41
Figure 2.21 Schematic showing attenuation of an electromagnetic wave by a conducting shield (thickness of shield = D).	43
Figure 3.1 Instrumental setup for measuring SE according to ASTM D4395-99.	55
Figure 3.2 Schematic process of chemical reaction between the oxidized HCMs and coupling agent.	56
Figure 3.3 FTIR spectra of hollow carbon microsphere: (a) oxidized HCMs, (b) Un-HC and (c) CA-HCMs.	58
Figure 3.4 Compression stress-strain curves of the syntactic foams with various amounts of (a) Un-HCMs and (b) CA-HCMs.	60
Figure 3.5 Comparison of compressive strength as a function of HCMs content.	61
Figure 3.6 Flexure stress-strain curves of the syntactic foams containing various amounts of (a) HCMs and (b) CA-HCMs.	63
Figure 3.7 Comparison of flexural strength as a function of hollow carbon microspheres content.	65
Figure 3.8 SEM micrograph of fracture surface of the syntactic foam after flexure tests.	65
Figure 3.9 Comparison of fracture toughness of the foams with various contents of hollow carbon microspheres.	67
Figure 3.10 Schematic of proposed fracture mechanisms of the syntactic foams: (a) crack deflection mechanism, (b) crack bowing mechanism and (c) debonding mechanism.	67
Figure 3.11 SEM micrograph of fracture surface of the syntactic foam containing 9.4 vol% Un-HCMs (a) and CA-HCMs (b) after fracture toughness tests.	69
Figure 3.12 SEM micrograph of fracture surface of the syntactic foam containing 46.9 vol% Un-HCMs (a) and CA-HCMs (b) after fracture toughness tests.	70
Figure 4.1 Flowchart of processing of the syntactic carbon foams.	75

Figure 4.2 Typical volume shrinkage (%) and weight loss (%) of the samples after being treated at different temperature.	78
Figure 4.3 Microstructure of the sample C900.	79
Figure 4.4 Typical Raman spectrums of C600 (B) and C900 (A).	80
Figure 4.5 Compressive and flexural strengths of treated samples.	85
Figure 4.6 Compression stress-strain curve of C200.	86
Figure 4.7 Compression stress-strain curve of C600.	86
Figure 5.1 Compressive yield strength of the CNFRSF containing various amounts of CNFs.	92
Figure 5.2 Compression stress- strain curve of the CNFRSF containing 1.5 vol% CNFs.	92
Figure 5.3 Compressive failure feature of the CNFRSF containing 1.5 vol% CNFs in the region 2 of the stress-strain curve.	93
Figure 5.4 Flexural strength of the CNFRSF containing various amount of CNFs.	95
Figure 5.5 SEM micrograph of fracture surface of the CNFRSF containing 0.5 vol% CNFs after flexural tests (low magnification).	95
Figure 5.6 SEM micrograph of fracture surface of the CNFRSF containing 0.5 vol% CNFs after flexural tests (high magnification).	96
Figure 5.7 Fracture toughness of CNFRSF containing various amount of CNFs.	98
Figure 5.8 SEM micrograph of fracture surface of the CNFs-free syntactic foam after fracture toughness tests.	98
Figure 5.9 SEM micrograph of fracture surface of the syntactic foam containing 2.0 vol% CNFs after fracture toughness tests.	99
Figure 5.10 SEM micrograph of fracture surface of the CNFRSF containing 2.0 vol% CNFs after fracture toughness tests.	99
Figure 5.11 EMI shielding effectiveness as a function of frequency for the CNFRSF with various CNFs content.	101

Figure 5.12 Relationships among CNFs content, electrical conductivity and EMI SE of the samples at 1.2 GHz.	101
Figure 5.13 Transmittance (T), reflectance (R) and absorbance (A) of EM radiation against the content of CNFs at 700 MHz.	102
Figure 6.1 Schematic process of chemical reaction among the oxidized HCM, the oxidized CNF and coupling agent of glutaric dialdehyde.	111
Figure 6.2 Schematic of proposed preparation process of syntactic foam containing copper coated HCMs (a) and nickel coated HCMs (b), respectively.	112

List of Tables

Table 1.1 Composite Components in Aircraft Applications [2].	2
Table 2.1 Data of isothermal curing of DGEBA/MP for various curing temperature [30].	13
Table 2.2 Curing condition of epoxy with various amines [31].	14
Table 2.3 Curing degree behavior of novolac resin [38].	17
Table 2.4 Curing degree behavior of resole resin [44].	19
Table 2.5 Mechanical properties of syntactic foams containing various volume fractions of glass microspheres (K46) and phenolic microspheres (BJO) [52].	21
Table 2.6 Product information of 3M hollow glass microspheres [53].	22
Table 2.7 Product information of hollow phenolic microspheres [58].	23
Table 2.8 Comparison of different hollow microspheres.	25
Table 2.9 Processing methods of syntactic foams.	28
Table 2.10 Mechanical properties of syntactic foams containing various hollow microspheres [52].	35
Table 2.11 Summarized mechanical properties of syntactic foams.	39
Table 2.12 Three EMI shielding mechanisms.	43
Table 2.13 Three factors affecting EMI shielding performance of polymer composites.	50
Table 3.1 The comparison of EMI SE value (frequency range from 30 MHz to 1.2 GHz)	71
Table 4.1 Electrical conductivity at room temperature for different samples.	80
Table 4.2 EMI SE values (frequency range from 30 MHz to 1.2 GHz).	82
Table 4.3 Skin depth and the contribution of reflection, absorption and multiple-reflections in the overall SE of C900 at different fixed frequency.	84

Table 5.1 Comparison of SE of CNFRSF and CNF composite containing same volume fractions of CNFs.	104
Table 5.2 Comparison of SE of CNFRSF and CNF composite as the phenolic resin matrix containing same volume fractions of CNFs.	104

List of Abbreviations

ASTM	American Society for Testing and Materials
CA-HCMs	Coupling agent treated hollow carbon microspheres
CB	Carbon black
CNF	Carbon nanofiber
CNFRSF	Carbon nanofiber reinforced syntactic foam
CNT	Carbon nanotube
DGEBA	Diglycidyl ether of bisphenol-A
HCM	Hollow carbon microsphere
HMTA	Hexamethylenetetramine
EMI	Electromagnetic interference
MP	Melamine phosphate
SE	Shielding effectiveness
Un-HCMs	Untreated hollow carbon microspheres
SEM	Scanning Electron Microscopy
XRD	X-ray diffraction
vol%	Volume Percentage
wt%	Weight Percentage

Chapter 1. Introduction

1.1 Background

Currently, various industries are spending large budgets on creating lighter, stronger and cheaper engineering materials. For example, in aerospace and automotive industries, engineers and scientists have paid a lot of attention to reduce the weight of cars and aircrafts through materials renovation. Reducing the weight would result in an increase in fuel efficiency. Better fuel efficiency of cars and aircrafts would make a greener environment as it could reduce the exhaust emission.

Compared with conventional metal-based engineering materials, polymer-based composite materials have gained popularity because of their light weight, flexibility, low costs and resistance to corrosion. Figures 1.1 shows the typical composite materials used in aircraft. In order to increase the fuel efficiency, composite materials are used in both passenger and military aircrafts to lower the weight of the structure. The components of the aircraft made out of composites for such aircrafts are shown in Table 1.1. For example, passenger aircraft Boeing 757 and 767 have composite parts, such as doors, rudders, elevators, fairings and spoilers to lower the weight, and hence increase the fuel efficiency and payload. It is also noted that carbon fibers are frequently introduced into polymer matrices, as shown in Figures 1.1. The purpose of the addition of carbon fibers is to enhance not only stiffness and strength, but also electrical conductivity of the composites. The high electrical conductivity leads to high electromagnetic interference (EMI) performance, which is also very important for aerospace applications.

Figure 1.1 Typical composite materials used in aircraft [1].

Table 1.1 Composite Components in Aircraft Applications [2].

Composite Components	
F-15	Horizontal and vertical tails, fins, rudders, speed brakes, stabilizer skins
F-16	Horizontal and vertical tails, fins, leading edge, skins on vertical fin box
Boeing 757	Doors, rudders, elevators, ailerons, spoilers, flaps, fairings
Boeing 767	Doors, rudders, elevators, ailerons, spoilers, fairings

Syntactic foam, which is synthesized by mechanical mixing of hollow microspheres (filler) with a matrix material (binder), is a special class of light weight composite materials that could facilitate a favorable combination of properties of their individual component. Various densities of syntactic foams can be achieved by changing the amount of hollow microspheres. The applications of syntactic foams have been found

in many areas, such as aerospace, marine, submarine [3] and ground transportation vehicle [4], because of their light weight, thermal stability and high stiffness. To enable wider applications of syntactic foams, it is essential to increase their mechanical properties, such as compressive strength, flexural strength and fracture toughness. For example, high fracture toughness can enable the syntactic foam to be employed in high-impact and damage-tolerant conditions.

Besides the enhancement in mechanical properties, the incorporation of functionality in syntactic foams could facilitate more applications. EMI shielding effectiveness (SE) is one of the important functional properties for advanced applications, such as electronic and military devices [5, 6]. The proper operation of electronic devices and electrical equipment depend strongly on the EMI shielding performance [7]. Poor EMI shielding performance could result in degradation in the performance of the devices and equipments or seriously threatening work place's safety. One of the published serious EMI incidents occurred on the USS Forrestal of Vietnam in July, 1967 [8]. It was reported that RF energy from a high powered ship's radar coupled into the firing circuits of an aircraft-mounted missile rocket motor, which ignited and fired the weapon into a number of other armed aircraft on the carrier flight deck. The resulting explosion and fire killed 134 people and caused \$ 72M of damage. Therefore, EMI shielding performance of materials is of huge concern especially for critical electronic systems. Noting that lightweight can be an important additional advantage to EMI shielding systems for some applications, syntactic foams with desired EMI SE properties become an attractive candidate for practical applications. However, SE enhancement of syntactic foams has relatively less reported in the literature. Therefore, development of syntactic foams with good mechanical properties and EMI shielding performance is essential.

1.2 Problem statement, hypothesis and objectives

In order to enhance their performance and further widen their applications, it is essential to develop syntactic foams with good mechanical properties yet low density. However, a decrease in density would usually be accompanied by a decrease in mechanical properties. A lower density resulting from the addition of more hollow microspheres leads to poorer mechanical properties because the hollow microspheres take up large volume of the composites. Studies have been reported that adding certain amounts of carbon fibers [9] or glass fibers [10] into syntactic foams can improve their mechanical properties. However, the addition of these fillers dramatically increases the density, i.e., destroys the main advantage of syntactic foams. Therefore, one of the objectives of this work is to improve the mechanical properties of syntactic foams while maintaining their low density. It is well known that the interface between filler and binder plays an important role in determining mechanical properties of the composite materials. Accordingly, it is expected that an enhancement in the interaction at the hollow microspheres-matrix interface would improve the mechanical properties of syntactic foams without sacrificing their main advantage. Besides the enhancement in the interaction between filler and binder, introducing small amounts of nano-fillers, such as carbon nanotube (CNT) and carbon nanofiber (CNF), would be an alternative method to improve the mechanical properties of syntactic foams. Compared with the micro-fillers, the use of nano-fillers in polymer composites allows system with low filler loading to obtain desired mechanical properties. Although the minor increase in density cannot be avoided, the mechanical properties of syntactic foams would dramatically increase.

In this study, EMI SE properties of syntactic foams will also be investigated. Due to the non-conductive nature of traditional polymer matrices and microspheres used in syntactic foams, EMI SE properties of syntactic foams have not been explored. Therefore, the other objective of this thesis is to develop conductive syntactic foams with EMI

shielding performance. In this work, hollow carbon microspheres (HCMs) instead of the traditional non-conductive hollow microspheres were used as the filler of syntactic foams. HCMs could create an electrically conductive network as long as they are connected each other. The use of coupling agent could improve the dispersion of conductive filler which may lead to the formation of electrical network within the matrix [11, 12]. Therefore, it was hypothesized that coupling agent could help to build a better electrical network for syntactic foams. In order to develop conductive syntactic foams, carbonization is an alternative approach because carbon matrix is a superior matrix than other non-conductive polymer matrix for EMI shielding applications due to its connectivity. Both closed electrical network and the low density of composites could be achieved by using carbon matrix instead of polymer matrix. Therefore, it is expected that syntactic foams could achieve desired EMI SE coupled with low density after carbonization. Besides the use of coupling agent and carbonization, introducing conducting nano-fillers, such as carbon nanofibers (CNFs), with low loading is an alternative method. Due to their larger aspect ratio, higher intrinsic conductivity and remarkable structures, adding small amounts of carbon nano-fillers could create an electrical network within the matrix with minor increase in density of syntactic foams.

1.3 Scope

In order to achieve the objectives, the work is divided into two parts: to improve the mechanical properties of syntactic foams (A) and to develop syntactic foams with EMI shielding performance (B). Three approaches were adopted, as shown in Figure 1.2.

Figure 1.2 Project outline.

The details of each approach are elaborated as follows:

- (C1) A method of coupling agent treatment of the surface of HCMs was developed. The effects of coupling agent on mechanical properties and EMI shielding performance were studied. The mechanical properties studied include compressive strength, flexural strength and fracture toughness. Various properties of the syntactic foams containing coupling agent treated HCMs were compared with that containing untreated HCMs. The coupling agent method will be presented in Chapter 3.
- (C2) A method of carbonization of the syntactic foams was developed. The effects of carbonization on mechanical properties and EMI shielding performance were

studied. Mechanical properties studied include compressive and flexural strengths.

The carbonization method will be described in Chapter 4.

- (C3) A method to process CNF reinforced syntactic foams was developed. The effects of the CNF content on mechanical properties and EMI SE were investigated. The mechanical properties studied include compressive strength, flexural strength and fracture toughness. This work will be presented in Chapter 5.

Chapter 2. Literature review

2.1 Introduction of syntactic foam

Syntactic foam is a special type of composite materials synthesized by filling a metal, ceramic or polymer matrix with hollow particles. It was developed in the early 60's and has been widely applied to aerospace and submarine industries [13-21]. The term "Syntactic" is derived from the Greek word "syntaktikos" meaning to "put together" [22]. The term "foam" is used because of the cellular nature of the materials. Figure 2.1 shows a sketch of syntactic foams. They are classified into two-phase and three-phase systems. Randomly dispersed hollow microspheres in the matrix give rise to two-phase syntactic foam, as shown in Figure 2.1 (a). During the processing of syntactic foams, air entrapment is possible, which leads to voids in the foam structure. The existence of voids in a two-phase system gives rise to a three-phase structure, which is shown in Figure 2.1 (b). The voids not only bring down the density but also reduce the strength of syntactic foam.

A scanning electron microscope (SEM) can be used to observe the microstructure of syntactic foams. Figure 2.2 shows a SEM image of syntactic foam. The voids are introduced into the matrix during the processing of syntactic foam. The hollow microspheres can be clearly seen as round particles embedded in the matrix. Half or more volume of hollow microspheres results in lower density of the syntactic foam.

Figure 2.1 A representative sketch showing (a) two phase structure involving matrix and microspheres and (b) three phase structure in the presence of voids [23].

Figure 2.2 SEM image of syntactic foam.

2.2 Materials used in syntactic foam

Various syntactic foams can be made as the matrices and fillers are usually made of different materials. This section discusses the materials that can be used as filler and binder of syntactic foams.

2.2.1 Binder

The matrix of syntactic foams can be made from polymers, metals or ceramics. In this review, the focus will be on the polymer-based syntactic foams. Thermosetting and thermoplastic polymers can be employed as the matrices of syntactic foams. Compared with the thermoplastic matrices, thermosetting ones have many advantages. For example, thermosetting polymer-based syntactic foams can be processed at much lower temperatures compared with thermoplastic ones, hence reducing the energy costs for processing. Also, thermoplastic syntactic foams have more solvent sensitivity and are

always affected by cleaning solutions [24]. Therefore, syntactic foams are mainly prepared by thermosetting matrices.

The thermosetting polymer resins used are phenolics, epoxies, cyanateesters, bismaleimides, unsaturated polyesters and polyurethanes. Among them, epoxies and phenolics are mainly used as the binders of syntactic foams. Diglycidyl ether of bisphenol-A (DGEBA) is a typical commercial epoxy resin and is synthesized by reacting bisphenol-A with epichlorohydrin in presence of a basic catalyst. Figure 2.3 shows the chemical structure of DGEBA resin. The properties of DGEBA resin depend on the value of n . The number of n represents repeating unit which is commonly known as degree of polymerization. Typically, n ranging from 0 to 25 is available in many commercial products. The cure kinetics of epoxy resins is highly dependent on the molecular structure of hardener. A wide variety of hardener for epoxy resins is available, such as amines and polyamides. Figure 2.4 shows chemical structure of diamine. When the DBEGA and diamine are mixed together, cross-linking structures will be formed, which results in a high strength and modulus structure as shown in Figure 2.5.

The curing kinetics of epoxy-amine reactions has been well established [25-28]. Primary and secondary amines are highly reactive with epoxy. The reaction of a primary amine (A_1) with an epoxy produces a secondary amine (A_2) which then reacts with another epoxy resulting in a tertiary amine (A_3). Tertiary amines are generally used as catalysts, commonly known as accelerators for cure reactions [29].

Figure 2.3 Chemical structure of diglycidyl ether of bisphenol-A.

Figure 2.4 Chemical structure of diamine.

Figure 2.5 Schematic process of chemical reaction between DGEBA and diamine.

Table 2.1 shows kinetic parameters obtained for DGEBA cured with melamine phosphate (MP). The chemical structure of MP is shown in Figure 2.6. It can be seen that the reaction order of the curing reaction at 200 °C is 1.84, which means the DGEBA/MP systems undergoes an epoxy-amine reaction at 200 °C. It can also be seen that the reaction orders become higher when the curing temperature increases. The higher reaction order is caused by the etherification of an epoxide ring and a hydroxyl group, which becomes significant at high curing temperature.

Table 2.1 Data of isothermal curing of DGEBA/MP for various curing temperature [30].

Curing temperature (°C)	Reaction rate constant (K·min ⁻¹)	Reaction orders		
		m	n	m+n
200	0.13	0.97	0.87	1.84
210	0.31	1.05	1.48	2.53
220	0.84	1.19	1.99	3.18
230	3.66	1.48	3.20	4.69

Figure 2.6 Chemical structure of melamine phosphate (MP).

Table 2.2 summarizes the curing condition of epoxy with various amines. The choice of amines depends on the application and the process selected.

Table 2.2 Curing condition of epoxy with various amines [31].

Name of hardener	Curing condition		Chemical structures
	Temperature (°C)	Time	
Tetraethylenepentamine (TEPA)	25-100	30 mins to 7 days	$\text{H}_2\text{N}-\text{CH}_2-(\text{NHCH}_2)_3-\text{NH}_2$
Diethylaminopropylamine (DEAPA)	65-115	1 to 4 hours	$\text{C}_2\text{H}_5-\text{N}(\text{C}_2\text{H}_5)-(\text{CH}_2)_3-\text{NH}_2$
N-aminoethylpiperazine (N-AEP)	25-200	30 mins to 3 days	$\text{H}_2\text{N}-(\text{CH}_2)_2-\text{N}(\text{CH}_2\text{CH}_2)_2-\text{NH}_2$
Isophoronediamine (IPDA)	80-150	4 to 5 hours
m-xylenediamine (m-XDA)	25-60	1 hours to 7 days
Metaphenylene diamine (MPDA)	80-150	2 to 4 hours
Diaminodiphenylsulfone (DDS)	80-150	2 to 4 hours

Except for epoxy resin, phenolic resin is also used as the matrix of syntactic foams. A key characteristic of phenolic resin is its ability to maintain structural and dimensional stability at high temperatures. When phenolic resin is exposed to temperature above its point of decomposition, it demonstrates higher char yield than other plastic materials. In

an inert environment, a structural carbon known as vitreous carbon will be converted from phenolic resin at high temperatures (normally above 600 °C). For these reasons, phenolic resin meets the challenges under high temperature environments in demanding applications such as aerospace.

Phenolic resin can be prepared by the reaction of phenols with formaldehyde. In an aqueous solution, formaldehyde exists in equilibrium with methylene glycol, as shown in Figure 2.7. Depending on the pH of the catalysts, two general resin types, novolac resin and resol resin can be formed [32]. Figure 2.8 shows the preparation process of novolac resin. It can be made where the molar ratio of formaldehyde to phenol is less than one. The initial reaction is between phenol and methylene glycol using acid-catalysis and then continues with additional phenol. The final novolac resin is able to react further with the addition of a hardener. The most common hardener is hexamethylenetetramine (HMTA), which is shown in Figure 2.9. It reacts with resin and phenol without producing huge amounts of free formaldehyde. Due to the multiple reaction sites involved, the cured phenolic resin possesses a complex three-dimensional network. The curing kinetics of novolac resin has been reported [33-37]. Table 2.3 exhibits the degree of curing at various temperature. It can be seen that, in the initial stage (400s), the curing process is independent on the curing temperature. However, the curing processes are different after 400s. When the curing time ranges from 700s to 750s, the curing process becomes much faster at 120 °C than that at 115 °C and 110 °C, which results from an great increase in both the cross-linking density and the molecular weight of the resin.

Figure 2.7 Chemical reaction of formaldehyde in aqueous solution.

Figure 2.8 Schematic preparation process of novolac resin.

Figure 2.9 Chemical structure of hexamethylenetetramine.

Table 2.3 Curing degree behavior of novolac resin [38].

Temperature (°C)	Time				
	400s	500s	600s	700s	750s
110	5%	7.5%	14%	18.5%	NA
115	5%	9%	18.5%	35%	42%
120	5%	11%	24%	56%	80%

Figure 2.10 shows the preparation process of resole resin. It can be made with a formaldehyde to phenol ratio of greater than one (usually around 1.5). The chemical reaction is catalyzed by, usually but not necessarily, a basic (alkaline) catalyst. The initial reaction is between phenol and methylene glycol to form methylol phenol. Methylol phenol can react with phenol to form a methylene bridge or react with itself to form a longer chain methylol phenolic. The resole resin is capable of being cured by the application of acids and heat. The cure process occurs through condensation of the methylol group (Figure 2.11). In some foam and foundry binder applications, a rapid cure of a resole resin is obtained at room temperature with strong acid. The curing kinetics of resole resin has been reported [39-43]. Table 2.4 exhibits the degree of curing at various temperature. It is obvious that the lower the curing temperature is, the longer the curing time is for a given degree of curing. Evidently, there are two pathways to reach the same degree of curing: (1) prolonging the reaction time to lower the reaction temperature and (2) increasing the curing temperature to shorten the reaction time. Figure 2.12 summarizes the preparation and curing conditions of novolac and resole resin.

Figure 2.10 Schematic preparation process of resol resin.

Figure 2.11 Curing reaction of resole resin.

Table 2.4 Curing degree behavior of resole resin [44].

Temperature (°C)	Time				
	2 mins	4 mins	6 mins	8 mins	10 mins
120	10%	18%	28%	33%	40%
130	15%	30%	41%	52%	60%
140	23%	46%	60%	71%	78%
150	41%	65%	78%	88%	91%
160	58%	82%	92%	97%	99%

Figure 2.12 Preparation and curing processes of phenolic resin.

2.2.2 Filler

The fillers used in syntactic foams are hollow particles. Hollow particles are available in various diameters ranging from millimeter to nanometer. So far, most of the literatures that have been reported on syntactic foams are based on microspheres. It is noted that the lower density of syntactic foams results from the introduction of hollow microspheres because the density of hollow microspheres is lower compared to that of resin binders.

Various types of hollow microspheres have been reported, such as ceramic [45], glass [46, 47], metal [48] and polymeric microspheres [49]. Glass microspheres are most frequently used due to their mechanical strength, smoothness and good wetting characteristics [50]. They can be made by heating tiny droplets of dissolved water glass using the “ultrasonic spray pyrolysis” method [51]. In general, syntactic foams containing glass microspheres exhibit better mechanical properties than those containing polymeric microspheres, such as phenolic microspheres, due to the substantial difference between the elasticity and modulus of glass and polymer [52]. Table 2.5 shows the mechanical properties of syntactic foams containing hollow glass microspheres and phenolic microspheres. It can be seen that both the compressive yield strength and fracture toughness of syntactic foams containing hollow glass microspheres are higher than those containing phenolic microspheres. It was reported that soda lime glass has a modulus about 77 GPa whereas phenol-formaldehyde has a modulus of about 6.8 GPa [52]. The difference in compressive yield strength is ascribed to the difference in modulus of two microspheres. Hollow glass microspheres can be produced by some manufacturers, such as 3M, Trelleborg Offshore and Saint Gobain. Table 2.6 exhibits product information of hollow glass microspheres from 3M. SEM image of 3M hollow glass microspheres is shown in Figure 2.13.

Table 2.5 Mechanical properties of syntactic foams containing various volume fractions of glass microspheres (K46) and phenolic microspheres (BJO) [52].

Syntactic foam	Compressive yield strength (MPa)	Fracture toughness (MPa·m^{0.5})
10 vol% K46	84.61	1.17
20 vol% K46	80.64	1.39
30 vol% K46	76.63	1.27
40 vol% K46	NA	0.95
50 vol% K46	NA	NA
10 vol% BJO	62.87	0.87
20 vol% BJO	51.08	0.99
30 vol% BJO	38.11	1.15
40 vol% BJO	31.39	0.92
50 vol% BJO	25.95	0.66

Table 2.6 Product information of 3M hollow glass microspheres [53].

	Product @ 3M	Density (g/cm ³)	Particle size distribution (μm)	Test pressure (Pa)
K Series	K1	0.125	30-120	250
	K15	0.15	30-115	300
	K20	0.20	30-105	500
	K25	0.25	25-105	750
	K37	0.37	20-85	3000
	K46	0.46	15-80	6000
S Series	S15	0.15	25-95	300
	S22	0.22	25-75	400
	S32	0.32	20-80	2000
	S35	0.35	20-80	3000
	S38	0.38	15-85	4000
	S38HS	0.38	19-85	5500
	S60	0.60	15-65	10000
	S60HS	0.60	12-60	18000

Figure 2.13 SEM image of hollow glass microspheres.

Polymeric microspheres are commonly made of epoxy resin, phenolics, silicone resin, unsaturated polyester resin, and so on [54, 55]. These microspheres are generally produced by viscous solutions and melts [56]. Among various polymeric microspheres, phenolic microspheres have been widely used for the filler of syntactic foams. They can be produced by some manufacturers, such as Asia Pacific Microspheres, Eastech Chemical, INC and Polyscience, INC. Table 2.7 shows product information of two types of hollow phenolic microspheres from Eastech Chemical, INC. SEM image of hollow phenolic microspheres is shown in Figure 2.14. Compared with hollow glass microspheres, lower density and better adhesion with polymeric matrices are the main advantages of phenolic microspheres. But they are always weaker and softer than glass microspheres [57].

Table 2.7 Product information of hollow phenolic microspheres [58].

Hollow phenolic microspheres	Density (g/cm³)	Particle size distribution (μm)	Test pressure (Pa)
BJO-840	0.25-0.35	5-127	1000
BJO-930	0.21-0.25	5-127	500

Figure 2.14 SEM image of hollow phenolic microspheres.

Carbon microspheres which are derived from phenolic microspheres or carbon pitch spheres are a special filler of syntactic foams. Carbon microspheres can be converted from phenolic microspheres by heating in an inert atmosphere to 800–1000 °C [24]. The density of carbon microspheres obtained is about 0.15 g/cm³. Report [56] has been shown that the syntactic foams containing HCMs could lead to better properties compared to that containing hollow glass microspheres. Furthermore, it has also been reported that the smaller the carbon microspheres, the stronger are the resulting foams [56]. Besides mechanical properties, HCMs syntactic foam systems have also been reported for the application of electromagnetic wave absorber due to their electrically conductive [59]. Figure 2.15 shows SEM image of HCMs, which produced from hollow phenolic microspheres. It can be seen that HCMs retained their spherical shape and only small amounts of them were broke, which proved the feasibility of this approach.

Table 2.8 compares three types of hollow microspheres. The choice of the microspheres depends on the proposed application.

Figure 2.15 SEM image of hollow carbon microspheres

Table 2.8 Comparison of different hollow microspheres.

	Hollow glass microspheres	Hollow phenolic microspheres	Hollow carbon microspheres
Density (g/cm³)	0.125-0.60	0.21-0.35	0.15-0.28 ^[24, 60]
Size distribution (μm)	12-120	5-127	5-500 ^[60]
Chemical compositions	Soda-lime-borosilicate ^[53]	Phenolic resin	Amorphous carbon
Processing methods	(1) Sol – gel processing ^[61] (2) Liquid droplet ^[51, 62] (3) Fly ash ^[63] (4) Rotating electrical arc ^[64] (5) Flame forming ^[65]	(1) In situ polymerization ^[66] (2) Spraying low viscosity solutions ^[67]	(1) Carbonization of hollow phenolic microspheres ^[60] (2) Pyrolysis of polystyrene-polyacrylonitrile blend ^[68]
Advantages	(1) Excellent water resistance (2) High strength-to-weight ratio (3) Non-combustible and non-porous (4) Available in a variety of sizes and grades	(1) Lower density (2) Superior compatability with resins (3) Improved flowability of resin matrix (4) Ablative Properties	(1) Lower density (2) Electrical conductive (3) Stable under high temperature (4) Easy in functionalization
Disadvantages	(1) Not compatible with polymer resin (2) Non-conductive	(1) Lower compressive strength (2) Available in few sizes and grades (3) Non-conductive	(1) Difficulty in preparation (2) High costs (3) Lower compressive strength

2.3 Preparation methods of syntactic foam

As described above, most of the syntactic foams are prepared with thermosetting polymer resins. These resins cure when mixed with hardener. A typical processing consists of mixing the hollow microspheres with the binder, pouring the mixture into the mold and curing the material [69]. Table 2.9 presents a brief summary of each process. A specific method used in the preparation of syntactic foams depends on the exact type of the microspheres and the binder.

A melt-mixing process is used when the resin is available in a powdery form. In this method, a solid mixture of the resin and hollow microspheres is prepared first. After that, the solid mixture is transferred to a mould of predetermined volume, melted and cured at high temperature [70]. Although the processing is easy to control, the airborne dust characteristic of microspheres poses environmental problems.

Solution processing is the most common methods for the production of syntactic foams. In this method, a dilute resin solution is mixed with the desired quantity of hollow microspheres using a low shear mixer. After removal of the solvent, the mixture is then manually filled into a mould and cured [55]. The advantage of this method is the reduction of air entrapment due to lower viscosity of the resin solution. However, it has many drawbacks. These include difficulty in the removal of the solvent before the final curing, introduction of health hazards of volatile solvents, and formation of defects when the solvent is evaporated by heat [71].

Two US patents [72, 73] described processing of syntactic foams from liquid resin without using solvent. Generally, the viscosity of the resin increases with the addition of the microspheres. High viscous resin is undesirable because it can prevent well dispersion and also prevent complete wetting of the microspheres. In this method, the desired quantity of hollow microspheres is mixed with the liquid thermosetting resin. The mixture is then heated to allow the resin to flow and wet the microspheres. After that, the mixture

is cured to form the syntactic foam. The advantage of this method is to prepare syntactic foams in the absence of solvent. However, the liquid resin does not produce highly wettability of the microspheres.

Syntactic foams have also been prepared by a coating method [74]. In this method, a thin film of resin solution is coated onto the surface of hollow microspheres. The coated microspheres are then vacuum filtered and rinsed with liquids. The purpose of liquids rinsing is not only to precipitate the resin onto the surface of microspheres, but also to remove the solvent by leaching. The uniform resin coated of hollow microspheres is achieved followed by vacuum drying. Finally, the coated microspheres are mixed with the liquid resin to form the syntactic foams.

A spraying method [75] has also been used for processing syntactic foams. Hollow microspheres and liquid resin are sprayed using the spray-up equipment. A liquid stream and a microspheres stream meet and mix in the air before entering the mould. The flow rate allows the operator to determine the density of the final syntactic foam.

Table 2.9 Processing methods of syntactic foams.

Processing methods	Advantages	Disadvantages
Melt-mixing	(1) Compatible with industrial processes ^[76] (2) Easy to disperse microspheres	(1) Damage of larger microspheres ^[77] (2) Airborne dust problem ^[24]
Solution processing	(1) Uniform dispersion of hollow microspheres (2) Reduction of air entrapment	(1) Difficulty in the entirely removal of the solvent (2) Introduction of volatile solvents (3) Formation of defects
Non solvent processing	Environment friendly	Difficulty in the production of highly wettability of hollow microspheres
Coating method	Uniform dispersion of hollow microspheres	Complex procedures
Spraying method	Difficulty in the control of flow rate	High costs

2.4 Mechanical behavior of syntactic foam

2.4.1 Compressive properties

Compression properties of syntactic foams have been reported by many researchers [15, 20, 78-88]. Gupta et al. [15] have identified three different regions which are shown in a typical compression stress-strain curve of syntactic foams, as shown in Figure 2.16. Region 1 shows a linear trend corresponding to the elastic behavior of the foam. At the end of region 1, the stress reaches the highest point which corresponds to the compressive yield strength of the foam. In Region 2, the stress becomes almost constant, which corresponds to the implosion of the hollow microspheres. At the end of region 2, the load further increases. A large number of microspheres get compacted and crushed, resulting in the densification of the foam. This is represented by region 3 of the curve. Gupta et al. [16, 86] studied the effect of the specimen size on the compressive properties of syntactic foams as well. It was observed that the specimen's behavior during compressive loading showed remarkable difference with respect to the aspect ratio. Figure 2.17 (a) shows the schematic representation crack origination and propagation for specimens with high aspect ratio. It was found that the cracks propagated through the center to the opposite face, giving rise to shear type of failure. However, as shown in Figure 2.17 (b), the crack propagation in the low aspect ratio specimens yielded wedge-shaped fragments from the sidewalls. A large central part of the specimen remaining intact and compressed uniformly was also found.

Figure 2.16 Compressive stress against engineering strain for syntactic foams.

Figure 2.17 Schematic representation of crack origination and propagation for specimens with (a) high aspect ratio and (b) low aspect ratio.

Besides the typical behavior of syntactic foams under compression, the properties of syntactic foams under the uniaxial compressive loading with varying volume fractions of fillers were also studied by many researchers. Wouterson et al. [52] reported that the specific compressive yield strength decreased with increasing filler content for K15 and phenolic microspheres. A similar decreasing trend in compressive yield strength with increasing filler content was reported by Palumbo et al. [13] and Lin and Jen [87] as well. Palumbo et al. studied the mechanical properties of a epoxy based syntactic foam containing hollow glass microspheres as a function of the weight content of the hollow microspheres. The failure of the syntactic foams was attributed to extensive debonding between the hollow glass microspheres and epoxy matrix. Li et al. [88] studied the compressive properties of epoxy based syntactic foam containing glass microspheres over a wide range of strain rates from $0.001 - 4000 \text{ s}^{-1}$. Since the epoxy matrix got stronger at higher rates, cracks propagation through microspheres began to dominate over the microspheres/matrix debonding under dynamic loading.

2.4.2 Flexural properties

Compared with the compressive properties of syntactic foams, the research on flexural properties is relatively scarce [3, 17, 52, 89-93]. Figure 2.18 shows a typical response of syntactic foam under three point bending. The behavior of syntactic foam can be qualified as being brittle. After achieving the maximum flexural load, an almost vertical drop in the load is observed. Wouterson et al. [52] reported that the flexural strength of the foam decreased with increasing filler content and was not affected by the component microspheres. A similar decreasing trend was observed by Tagliavia et al. [93] as well. Furthermore, it was studied that the flexural properties of composites containing vinyl ester-glass hollow-particle. The results showed that the flexural modulus was higher

as compared with the neat resin though the flexural strength decreased with increasing filler content. Moreover, the specific modulus was also higher than that of the neat resin, providing the possibility of weight saving in structural applications.

Figure 2.18 Flexural stress against engineering strain for syntactic foams.

2.4.3 Fracture toughness

Fracture toughness is one of the most attractive parameters of syntactic foams. It is quantified by the stress intensity factor, K , which relates the local stress near the crack tip to the remote stress and specimen geometry [57]. As the stress intensity factor increases and reaches a critical value, K_{Ic} , the crack will grow [94]. High fracture toughness allows the use of syntactic foams in high-impact and high damage-tolerant conditions. Wouterson et al. [49] assessed the fracture toughness, K_{Ic} , of syntactic foam containing glass microspheres (k46) with different densities as a function of microsphere content. The results showed that K_{Ic} increased with increasing content of glass

microspheres, and the increase in K_{Ic} was relatively higher compared to the decrease in density which resulted from the addition of microspheres. A similar trend was observed by Lee and Yee [95] as well. It was revealed the fracture process of glass beads/epoxy resins composites by changing the volume fraction of glass beads. The fracture toughness generally increased with increasing the content of glass beads. Wouterson et al. [96] studied the influence of the foam microstructure on the specific fracture properties as well. It was noted that the specific fracture toughness of syntactic foam depended on the volume fractions of added microspheres. The increase in K_{Ic} reached a maximum value (near 30 vol% of microspheres) after which the decrease trend was observed. The changing trend in K_{Ic} was attributed to a change in the dominant toughening mechanisms from crack front bowing and filler stiffening to excessive debonding of microspheres.

2.5 Factors affecting the mechanical properties of syntactic foam

Mechanical properties of syntactic foams are affected by several factors. In this section, volume fraction, microspheres/matrix adhesion and fiber reinforcement effect will be reviewed in detail.

2.5.1 Volume fraction of microspheres

Properties of syntactic foams, such as compressive strength, flexural strength and fracture toughness, are affected by the volume fraction of microspheres. In general, the density of microspheres is much lower than that of matrices. Hence, the density of syntactic foam is inversely proportional to the volume fraction of microspheres. Wouterson et al. [52] studied the mechanical properties of syntactic foams containing three different types of microspheres with various volume fraction. The data is shown in Table 2.10. It was found that the compressive and flexural strengths decreased with increasing microspheres content. The decrease trend is attributed to the introduction of

more air spaces from the inside of the hollow spheres in the syntactic foam. These air spaces take up a large volume of the matrix, which weaken the overall strength of the whole structure thus reduces the mechanical properties of syntactic foams. A similar trend was observed by Kishore et al [97]. Compressive properties of syntactic foams containing hollow glass microspheres with varying of microspheres volume fraction was studied. It was concluded that the compressive strength, modulus and density of syntactic foams decreased as the volume fraction of the microspheres increased.

Compared with compressive and flexural strengths, the behavior of fracture toughness was dissimilar. It can be seen that fracture toughness increases up to 30 vol% and decreases beyond 30 vol% of filler content for all types of microspheres. A similar trend for the fracture toughness has also been reported for other composites [98]. The increase in fracture toughness indicates the presence of a toughening mechanism which increases the fracture energy compared to neat resin. The decrease in fracture toughness beyond 30 vol% could be suggesting a change of dominant fracture mechanism. The toughening from 0 to 30 vol% microspheres is affected by a combination of the crack bowing mechanisms and the filler stiffening effect. When the content of microspheres increases beyond 30 vol%, the microspheres could not be completely wetted by the resin. More debonded microspheres are present, which results from inter-sphere sliding and stress concentration. Therefore, debonding of microsphere is the dominant mechanism when the content of microspheres increases beyond 30 vol%. The existence of more debonding microspheres leads to reduce the fracture toughness.

Table 2.10 Mechanical properties of syntactic foams containing various hollow microspheres [52].

Volume fraction of microspheres	Compressive yield strength (MPa)	Flexural strength (MPa)	Fracture toughness (MPa·m^{0.5})
10% K15	52.95	56.61	0.95
20% K15	54.18	43.63	1.20
30% K15	44.73	27.67	1.16
40% K15	37.96	25.59	0.94
50% K15	31.17	22.51	0.71
10% K46	84.61	53.32	1.17
20% K46	80.64	36.04	1.39
30% K46	76.63	31.38	1.27
40% K46	NA	33.99	0.95
50% K46	NA	33.99	NA
10% BJO	62.87	60.47	0.87
20% BJO	51.08	46.70	0.99
30% BJO	38.11	38.91	1.15
40% BJO	31.39	31.52	0.92
50% BJO	25.95	27.22	0.66

2.5.2 Matrix/microspheres adhesion

The mechanical properties of syntactic foams are directly dependent on the characteristic filler-binder interface. The level of stress transfer across the interface from filler to matrix is determined by the strength of the adhesive bond between microspheres and matrix. In many systems, the matrix is the only load carrier and little stress is transferred to the microspheres due to the poor adhesion. In order to improve the adhesion, it is possible to use coupling agents which could create chemical bonds between

microspheres and matrix and then allow the microspheres to act as reinforcements under loading. Silanes are often used as a coupling agent to enhance the interfacial strength in glass-polymer systems [99]. The syntactic foam containing silane coating A16 microspheres exhibited 25% higher strength than that containing untreated B38 microspheres under flexural loading, even though B38 has an isostatic crush pressure eight times that of the A16 [100]. Rutz and Berg [57] suggested that the adhesive bond between microspheres and matrix played an important role in determining the mechanical properties of syntactic foam as long as the failure mechanism was debonding in the syntactic foams.

2.5.3 Fiber reinforcement effect

In order to widen the application of syntactic foams, several strategies have been devoted to improving the mechanical properties of syntactic foams by fiber reinforcement. The fiber reinforced syntactic foams are usually made by using commercially available microspheres and low volume fractions of short fibers. Short fibers normally served to enhance the strength of the matrix with minimal weight penalty. Karthikeyan et al. [101] added 5 wt% of glass fibers to syntactic foam containing glass microspheres, improving compressive strength by 15-20 and flexural strength by 30% with the addition of 3 wt% fibers. Bibin and co-workers investigated the effect of glass fiber on the mechanical properties of cyanate ester syntactic foams [102]. Flexure strength increased with fiber concentration and reached a maximum at a fiber loading of 16.6 wt%. The increase in strength is ascribed to the load-bearing capacity of the fibrous reinforcement, which are very effective in transferring the load from the matrix. Wouterson et al. [9] examined the effect of short carbon fibers reinforcement on the mechanical properties of syntactic foams. Results showed that the fracture toughness increased by 95% for the hybrid

reinforced composites. Figure 2.19 [103] shows the SEM image of the fracture surface of short carbon fiber reinforced syntactic foam. Fractured and debonded fibers are clearly observed. It is obvious that the matrix around the short carbon fibers shows increased deformation compared to areas without fibers. Plastic dilatation of matrix occurs when the fibers debond, which results from the effective load transfer from fibers to matrix.

Figure 2.19 SEM image of the fracture surface of short carbon fiber reinforced syntactic foam.

The method of processing of fiber reinforced syntactic foams has a profound influence on their mechanical properties. Karthikeyan et al. [104] prepared the syntactic foam containing 3.54 wt% fiber in two ways. In the first method, microspheres were added to the resin first, followed by the fiber. In the second method, fibers were added to the resin first before the microspheres. The results showed that the flexural modulus of syntactic foam prepared by the first method is lower than that prepared by the second

method. In the first method, the microspheres act as an obstacle for the distribution of fibers. Therefore, the fibers were less effective in bearing the load transferred from the matrix.

The length of fiber is also an important factor affecting the mechanical properties of fiber reinforced syntactic foams. Bibin et al. [102] investigated the effect of fiber length (5-25mm) on the flexural strength of fiber reinforced syntactic foam. Results showed that the flexural strength increased with fiber length and reached a maximum at a fiber length of 20mm. Further increase in fiber length led to a decrease in flexural strength. The increase in flexural properties is attributed to the effective load transfer along the length of the fiber. The area of a single fiber in contact with the resin matrix increases if the fiber length increases. As a result, the load can be more effectively carried throughout the length of the fiber. When the fiber length increases beyond 20mm, the fiber may curl. This leads to a reduction in the effective fiber length in the direction of the applied load, which results in the decrease in flexural strength.

2.6 Summary of mechanical properties of syntactic foam

The mechanical properties of syntactic foams, such as compressive properties, flexural properties and fracture toughness have been introduced in section 2.4. Three factors affecting the mechanical properties include volume fractions of microspheres, interfacial adhesion between filler and matrix and fiber reinforcement have also been discussed in section 2.5. Table 2.11 summarizes conclusions and mechanisms that drawn from the literature review.

Table 2.11 Summarized mechanical properties of syntactic foams.

Mechanical properties	Factors affecting the mechanical properties		
	Volume fraction of microspheres	Matrix/microspheres adhesion	Fiber reinforcement
Compressive properties	Higher volume fractions of microspheres allows more air spaces taking up in the matrix, which cause the reduction of compressive and flexural strengths Toughen mechanism: (1) Below 30 vol% of microspheres: Filler stiffening effect and crack bowing (2) Beyond 30 vol% of microspheres: Debonding of microspheres Maximum facture toughness: 30 vol% of microspheres	The strength of the adhesive bond between the microspheres and the matrix determines the level of stress transfer across the interface.	The mechanical properties of fiber reinforced syntactic foam can be controlled by the (1) Volume fractions of fiber (2) Processing parameters (3) Fiber length.
Flexural properties		The introduction of coupling agent can improve the adhesion.	
Fracture toughness		Coupling agent creates good interfacial adhesion which needs more energy to break and thus improve the mechanical properties.	

2.7 EMI SE of polymer composites

2.7.1 EMI shielding theory and mechanism

Electronic products need packaging to get an adequate mechanical protection to avoid possible damage before they are delivered to the end users. The packaging of electronic devices is also required to maintain an adequate EMI shielding to not only avoid the leakage of unintended electromagnetic (EM) radiation from the enclosed electronic circuits, but also protect the enclosed circuits from the external interference emission.

EMI shielding refers to the reflection and/or adsorption of EM radiation by a material, which thereby acts as a shield against the penetration of the radiation through the material. The EMI shielding capability of a material is called shielding effectiveness (SE). The SE of a material is defined in terms of the ratio between the incoming power (P_i) and outgoing power (P_o) of an EM wave as [105]:

$$SE = 10 \log(P_i / P_o) \quad (2.4)$$

The unit of SE is given in decibels (dB). Figure 2.20 illustrates the reflection and transmission of the EM wave upon a material. The uniform EM wave with the electric field E_i and magnetic field H_i is normal incident to the material from the left side. When the EM wave strikes the left side of the material, parts of the EM wave are reflected in the opposite direction with electric field E_r and magnetic field H_r . Other parts of the EM wave are transmitted through the material with electric field E_t and magnetic field H_t . Therefore, the electric field SE can be expressed as:

$$SE = 20 \log(E_i / E_t) \quad (2.5)$$

The magnetic field SE can be expressed as:

$$SE = 10 \log(H_i / H_t) \quad (2.6)$$

Figure 2.20 EM plane wave is normal incident to a material with thickness D .

Three mechanisms for EMI shielding have been reported thus far [106-109]. The primary mechanism of EMI shielding is reflection. To facilitate reflection, the materials must possess mobile charge carriers (electrons or holes) to interact with the incoming EM wave. Absorption is the second important mechanism. It is caused by the loss of heat as the electromagnetic wave crosses the barrier, and is dependent on the thickness of the shield materials. For significant absorption, the shield materials should possess electric and/or magnetic dipoles which could then interact with the EM fields. The third shielding mechanism is multiple-reflections, which operates via the internal reflections within the shielding material. Therefore, the overall SE is the sum of all the three terms:

$$SE_{overall} = SE_R + SE_A + SE_{MR} (dB) \quad (2.7)$$

Figure 2.21 illustrates the shielding mechanisms in a conductive plate. When an EM wave strikes a homogenous conductive material, two waves will be created at the

external conductive surface; a reflected wave and transmitted wave. As the transmitted wave propagates in the conductive shield, the amplitude of the wave exponentially decreases. The decrease phenomenon results from absorption and the energy loss due to the absorption will be dissipated as heat [108]. Once the transmitted wave reaches the second surface of the shield (D), a portion of wave continues to transmit from the shield, and a portion will be reflected into the shield. The portion of internal reflected wave will be re-reflected within the shield. The internal reflection represents the multiple-reflections mechanism. Typically, the effect of multiple-reflections to the overall shielding depends on the skin effect. The strength of an EM wave decreases exponentially as it penetrates a conductive material. The depth at which the electric field drops to $(1/e)$ of the incident strength is call the skin depth (δ), which is given as follows [107]:

$$\delta = (\pi f \sigma \mu)^{-1/2} \quad (2.8)$$

where f is frequency (Hz), and $\mu = \mu_0 \mu_r$, $\mu_0 = 4\pi \times 10^{-7}$ is the absolute permeability of free space (H/m), and σ is the electrical conductivity (S/m). If the shield is thicker than the skin depth, the multiple-reflections can be ignored. However, the effect of multiple-reflections will be significant as the shield is thinner than the skin depth. The effect of multiple-reflections that affects the overall SE can be calculated by [108]:

$$SE_{MR} = 20 \log |1 - e^{-2/\delta}| \quad (2.9)$$

Equation 2.9 shows that the SE of multiple-reflections is a negative term. Therefore, it reduces the overall SE. The comparison of three EMI shielding mechanisms is presented in Table 2.12.

Table 2.12 Three EMI shielding mechanisms.

Reflection	Absorption	Multiple-reflections
(1) Positive to overall SE	(1) Positive to overall SE	(1) Negative to overall SE
(2) Possess mobile charge carriers (electrons or holes).	(2) Dependent on the thickness (D) and skin depth (δ) of the shield.	(2) Enhance by large surface or interface areas.
(3) Increase with increasing the conductivity of the shield.	(3) Enhance when the shielding material has electrical or magnetic dipoles.	(3) If $D > \delta$, can be ignored. If $D < \delta$, cannot be ignored.

Figure 2.21 Schematic showing attenuation of an electromagnetic wave by a conducting shield (thickness of shield = D).

2.7.2 SE model for composites

Composites are made up of the guest materials and the host material. In this study, the guest materials are HCMs and CNFs, respectively. The host material is the insulated plastic matrix: phenolic resin. The EMI SE of composites can be measured experimentally, and it also can be calculated theoretically according to the ratio of incident EM wave to the transmitted EM wave. The effective relative permittivity $\mathcal{E}_{eff}$ of composites is the very important parameter within the calculation. It can be approximately calculated from the Maxwell Garnett formula [110]. The $\mathcal{E}_{eff}$ of composites can be expressed as:

$$\mathcal{E}_{eff} = \mathcal{E}_e + 3f\mathcal{E}_e \frac{\mathcal{E}_i - \mathcal{E}_e}{\mathcal{E}_i + 2\mathcal{E}_e - f(\mathcal{E}_i - \mathcal{E}_e)} \quad (2.10)$$

where $\mathcal{E}_e$ is the relative permittivity of the matrix, $\mathcal{E}_i$ is the relative permittivity of the inclusion and f is the volume fraction of the inclusion. If the inclusions are electrical conductive particles, the relative permittivity $\mathcal{E}_i$ can be expressed as [111]:

$$\mathcal{E}_i = \mathcal{E}' - j\mathcal{E}'' = \mathcal{E}' - j \frac{\sigma}{\omega\mathcal{E}_0} \quad (2.11)$$

where $\mathcal{E}'$ and $\mathcal{E}''$ are the real and imaginary part of the complex relative permittivity of the inclusion, respectively. σ is the electrical conductivity of the inclusion.

As shown in Figure 2.21, the transmission coefficient T can be expressed as [111]:

$$T = \frac{T_1 T_2 e^{-\gamma_m D}}{1 + R_1 R_2 e^{-2\gamma_m D}} \quad (2.12)$$

where T_1 and T_2 are the transmission coefficients at the boundary 0 and the boundary D, respectively. R_1 and R_2 are the reflection coefficients at the boundary 0 and the boundary D, respectively. γ_m is the complex propagation constant. D is the thickness of the shield material. The T_1 , T_2 , R_1 , and R_2 can further be expressed in terms of the impedance Z :

$$T_1 = \frac{2Z_m}{Z_m + Z_0} \quad (2.13)$$

$$T_2 = \frac{2Z_0}{Z_m + Z_0} \quad (2.14)$$

$$R_1 = \frac{Z_m - Z_0}{Z_m + Z_0} \quad (2.15)$$

$$R_2 = \frac{Z_0 - Z_m}{Z_m + Z_0} \quad (2.16)$$

where Z_0 and Z_m are the impedance of the air and the composite material, respectively. Z_0 and Z_m can further be expressed as:

$$Z_0 = \sqrt{\frac{\mu_0}{\epsilon_0}} \quad (2.17)$$

$$Z_m = Z_0 \sqrt{\frac{\mu_r}{\epsilon_{eff}}} \quad (2.18)$$

The propagation constant γ_m can be expressed as [111]:

$$\gamma_m = j\omega \sqrt{\epsilon_0 \mu_0 (\epsilon'_{eff} - j\epsilon''_{eff})} \quad (2.19)$$

So the SE can be calculated in terms of T ,

$$SE = -20 \log(|T|) \quad (2.20)$$

2.7.3 Polymer composites for shielding

Metals are the most commonly used for EMI shielding applications because of their excellent SE. The mechanism of EMI shielding of metals is mainly reflection which is due to the free electrons in them [107]. However, in order to reduce weight and other desirable properties, metals are increasingly replaced with polymer composites. Compared to traditional metal-based EMI shielding materials, conducting polymer-matrix

composites have many advantages for EMI applications such as flexibility, light weight, resistant to corrosion and low cost [112]. The polymer matrix does not contribute to EMI shielding due to its non-conductive nature. However, it can affect the connectivity of the conductive filler and hence enhances the EMI shielding performance.

Various conductive fillers have been used to fabricate composites for EMI shielding applications including carbon black (CB) [113, 114], carbon fiber [115-118], nickel filament [119], stainless steel fiber (SSF) [120] and copper fiber [121]. For example, Das et al. [113] worked on the EMI shielding characteristics of ethylene-vinyl acetate and natural rubber filled with CB and short carbon fiber. It was found that the CB filled composites exhibit lower SE compared with CF filled ones. The SE of 20 dB was obtained for the composites containing CF in X-band region. Luo and Chung [118] reported that the SE of composites with continuous carbon fibers was higher than those with discontinuous fillers. Bagwell and coworkers [121] investigated the EMI SE of copper fiber/epoxy composites. Results showed that the addition of copper fibers with the correct fiber shape and surface treatment to epoxy matrix resulted in a multifunctional composite which significantly improved the SE and the electrical conductivity.

2.8 Approaches on improving the SE performance

The EMI shielding performance of polymer composites is affected by several factors, such as dispersion of filler, carbon matrix and nanofiber reinforcement effect, which will be reviewed in detail.

2.8.1 Dispersion of conductive filler

Uniform dispersion of conductive filler plays an important role in performing good conductivity of composites. Higher electrical conductivity leads to higher SE.

However, very few studies have been reported on the relationship between dispersion behavior of filler and EMI SE. Chiang and Chiang [122] investigated the SE of composites with nickel-coated carbon fibers treated with a titanate coupling agent. It was found that the EMI SE was improved when the carbon fiber was coupled with titanate. The addition of a coupling agent improved the dispersion of carbon fiber and hence formed better network conductive paths. Im and coworkers [123] reported that the dispersion of CB in electrospun carbon fiber enhanced by fluorination. A hydrophobic surface group was introduced on CB. The resultant electrical conductivity of carbon composites sheet reached 38 S/cm and a high EMI SE of 50 dB was obtained. Li and coworkers [124] studied the EMI SE of poly(L-lactide) (PLLA) /silsesquioxane grafted multiwalled carbon nanotubes (MWCNTs) composite. Homogeneous dispersion of silsesquioxane grafted MWCNTs occurring throughout the polymer resulted in higher electrical conductivity. High EMI SE (15–16 dB) was obtained in the 36–50 GHz range at 4 wt% filler loading.

2.8.2 Carbon matrix

Compared with polymer matrix composites, carbon matrix composites are superior in EMI shielding due to their high conductivity [107]. However, reports on EMI shielding performance of carbon matrix composites are scarce. Luo and Chung [118] studied the EMI shielding using continuous carbon fiber carbon matrix and polymer matrix composites. It was found that continuous carbon fiber composite with carbon matrix was more conductive than that with epoxy matrix. Carbon matrix composites were effective for shielding. The EMI SE of carbon matrix composite reaches 124 dB at 0.3 MHz - 1.5 GHz. Wen and Chung [125] investigated pitch-matrix composites for EMI shielding application. SE of around 25 dB was observed at 1.0 GHz. Liu et al. [126]

reported EMI SE of amorphous carbon matrix composites with interconnected carbon nano-ribbon networks in the frequency range of 30 KHz – 1.5 GHz. It was observed that sintering temperature played a significant role on the SE and the conductivity of the samples. The higher the sintering temperature, the higher the electrical conductivity and the SE would be. The SE value reached 44.3 dB at 800°C at 1.0 GHz.

2.8.3 Nanofiber reinforcement effect

The addition of high aspect ratio electrical conducting nanofiller into polymer matrix is an effective approach for creating conducting polymer nanocomposites, which in turn are suitable for EMI shielding applications. Compared with carbon fiber, CNF possesses higher mechanical strength, aspect ratio and conductivity and smaller diameter. Hence, it has emerged to be an excellent option for high-performance EMI shielding materials at low filler loading [127, 128]. However, very few studies have been conducted to evaluate the EMI shielding performance of CNF composites. Lee and coworkers [129] studied the EMI SE of 40 wt% CNF filled poly(vinyl alcohol) and compared it to that of 40 wt% CB filled poly(vinyl alcohol). It was found that although the SE of CNF/poly(vinyl alcohol) film was lower than that of CB/poly(vinyl alcohol) film, the SE of CNF/poly(vinyl alcohol) film was higher after heat treating the CNF. Yang et al. [128] evaluated the EMI SE of CNF reinforced liquid crystal polymer composites. It was observed that the EMI SE increased with increasing CNFs loading in the frequency range of 0.15 – 1.5 GHz and 41 dB of SE was achieved. The main shielding mechanism of the composites was surface reflection and multiple-reflections. Zhang and coworkers [130] investigated the EMI SE of CNF/polyesterpolyol shape memory polymer composites with different CNFs weight fraction and frequencies. The experiments to evaluate EMI SE were carried out in K-band (8 - 26.5 GHz), Q-band (33 - 50 GHz) and V-band (50 – 75

GHz) frequency ranges. The SE of 6.7 wt% CNF/SMP was 35 dB at 26 GHz while it was 60 dB at 75 GHz. It was also found that EMI SE increased with increasing thickness of the shielding materials. For instance, SE increased from 16 to 35 dB in the K-band as the thickness of the shielding materials was increased from 0.5 to 3 mm. This observation indicated that contribution of absorption to the overall SE was highly influenced by the thickness of the shielding materials. Al-Saleh and Sundararaj [131] studied the EMI SE of different CNF-filled polymers and polymer blends. For example, the SE of 30 dB was observed for 7.5 vol% CNF/PE composite with 2mm thickness over a frequency range of 50 – 1500 MHz.

2.9 Summary

Currently, the mechanical properties of syntactic foams have been receiving considerable attention due to their higher strength/weight ratio compared to the polymer composites. Several factors can influence the mechanical properties of syntactic foams, such as the volume fraction of the filler, interfacial adhesion between filler and matrix and fiber reinforcement. The details have been presented in Table 2.11.

EMI SE has already been studied in the area of polymer composites. Various approaches have been found to improve the SE performance of polymer composites, such as well-dispersed conductive filler, using carbon matrix instead of insulated matrix and carbon nanofiber reinforcement. Table 2.13 presents three factors affecting EMI shielding performance of polymer composites.

Table 2.13 Three factors affecting EMI shielding performance of polymer composites.

Dispersion of conductive filler	Carbon matrix	Carbon nanofiber reinforcement
The electrical conductivity is enhanced by the uniform dispersion of conductive filler, which leads to the improvement of SE.	High conductive carbon matrix enhances the connectivity of the filler, which leads to high electrical conductivity and thus improves SE performance.	High aspect ratio and intrinsic conductivity of CNF lead to high electrical conductivity and thus high EMI shielding of composites with low filler loading.

Based on the literature review, there are considerations to further develop syntactic foams

(1) The creation of interfacial bond between filler and matrix could not only improve the mechanical properties, but also enhance SE performance.

(2) Highest EMI SE and/or mechanical properties of syntactic foam can be obtained by the addition of appropriate amount of filler.

(3) Conductive syntactic foam can be obtained by using high conductive carbon matrix instead of non-conductive polymer matrix.

(4) The addition of small amount of CNFs leads to high mechanical properties and EMI SE of polymer composites.

Chapter 3. Effect of coupling agent on mechanical properties and EMI shielding performance of syntactic foams

3.1 Introduction

It is well known that the interaction at the filler-binder interface plays a significant role in improving the mechanical properties of composite materials. It has been proven that the mechanical properties of composite materials will be improved with the use of a suitable coupling agent. However, most of the researches have restricted to carbon fiber and epoxy-based composite materials systems [11, 132, 133]. The effect of coupling agent is rarely used for improving the mechanical properties of syntactic foams. In addition, the conductivity of composite materials is highly dependent on the uniform dispersion of conductive fillers, and the dispersion of conductive fillers may also be enhanced by the use of coupling agent as well. Due to the traditional non-conductive microspheres used in syntactic foams, conductive syntactic foams have not been explored so far.

In this chapter, hollow carbon microspheres (HCMs), instead of traditional non-conductive microspheres, were used as the filler because of the conductive nature of the HCMs. The HCMs were produced from hollow phenolic microspheres. Phenolic-based syntactic foams containing HCMs were investigated. The effects of a coupling agent, glutaric dialdehyde, on mechanical properties and EMI SE of the syntactic foams were investigated. The mechanical properties investigated include compressive strength, flexural strength and fracture toughness. The mechanisms for the mechanical property enhancement and SE property will also be discussed.

3.2. Materials and experimental procedures

3.2.1 Raw materials

The syntactic foams were prepared by mechanical mixing HCMs with phenolic resin. HCMs were produced from the raw hollow phenolic microspheres (BJO-093, Asia pacific/Eastech). They can be formed by heating the raw hollow phenolic spheres at a rate of 5 °C/min and dwelt at a 900 °C for 3 h in an argon atmosphere. Phenolic resin was purchased from International laboratory, USA.

3.2.2 HCM surface treatment

The HCMs were ultrasonically cleaned in acetone for 30 minutes. After cleaning, the microspheres were subjected to oxidation in 65% nitric acid (Sigma-Aldrich) for 5 h at 25 °C, followed by filtering and washing with distilled water and then dry in a vacuum oven at 50 °C. A coupling agent, glutaric dialdehyde (Sigma-Aldrich), was used to generate interfacial chemical bonds. 10 g of oxidized HCMs was immersed in 90 g of coupling agent solution for 24 h. The treated HCMs were then filtered and washed with distilled water and dried in a vacuum oven at 50 °C. The untreated and coupling agent treated HCMs were labeled as Un-HCMs and CA-HCMs, respectively.

3.2.3 Preparation of syntactic foam

Un-HCMs and CA-HCMs with 9.4 vol%, 18.8 vol%, 28.1 vol%, 37.5 vol% and 46.9 vol% were added to the phenolic resin in multiple steps to avoid agglomeration. In order to minimize gas bubbles in the phenolic resin, the mixture was stirred slowly. After that, the syntactic foam was poured to a mold, which was then left under a constant pressure of 2.0 MPa for 24 h to cure at room temperature.

3.2.4 Fourier transformed infrared (FTIR) spectrometer

FTIR (PerkineElmer Instruments Spectrum GX) was utilized to detect the chemical bonding between the HCMs and coupling agent groups. The spectrum obtained was scanned from 4000 to 500 cm^{-1} .

3.2.5 Mechanical tests

Three tests were performed on the mechanical properties of the foams. For compression tests, the specimens were machined to blocks of $25.0 \times 25.0 \times 12.0 \text{ mm}^3$ according to ASTM Standard C365/C 365M – 05. The tests were carried out at room temperature by using an Instron Tester (Model 4206), which has a maximum capacity of 100 KN. The cross-head speed applied was 0.5 mm/min. The compressive yield strength σ_c was calculated by

$$\sigma_c = \frac{P}{A}, \quad (3.1)$$

where σ_c is the compressive yield strength, P is the load at yield, and A is the cross-sectional area. All the results were average of five tests.

For flexural tests, syntactic foams were machined to specimens in dimensions of $127.0 \times 12.7 \times 3.0 \text{ mm}^3$. The tests were performed using an Instron Tester (Model 5567), which has a maximum capacity of 30 KN. The strain rate was maintained at 0.01/min. The cross-head speed, z , was calculated by

$$z = \frac{R \times S^2}{6d}, \quad (3.2)$$

where R is the strain rate, S is the span of the support, which was chosen to be 48 mm, and d is the depth of the sample. All the results were calculated based on the average of five tests. The equation of the cross-head speed was recommended according to ASTM Standard D790-07.

For fracture toughness tests, single-edge notched bending specimens were loaded on a three-point bending setup. For all specimens, the notch length, a , was measured to be between 0.5 and 0.6 times the specimen width, W . The notch width was 0.015 W or thinner. The tests were performed by an Instron Model 5567 at a cross-head speed of 5 mm/min. The specimen dimensions were $60.0 \times 12.7 \times 6.35$ mm³, which satisfies the requirement for plane strain conditions [134]. The fracture toughness, K_{Ic} , can be estimated from the following equations [95]:

$$K_{Ic} = Y \frac{3LS\sqrt{a}}{2tW^2}, \quad (3.3)$$

$$Y = 1.93 - 3.07\left(\frac{a}{W}\right) + 14.53\left(\frac{a}{W}\right)^2 - 25.11\left(\frac{a}{W}\right)^3 + 25.80\left(\frac{a}{W}\right)^4, \quad (3.4)$$

where Y is a geometry correction factor, L is the peak load at the onset of crack growth in a linear elastic fracture, t is the specimen thickness, W is the width of the specimen, S is the support span and a is the crack length.

3.2.6 SE measurements

To quantify the EMI shielding performance of a planar material, the SE of the material under test can be measured with the test setup in accordance with ASTM D4935-99 method, as shown in Figure 3.1 [50, 135, 136]. The signal source (Port 1) of the Vector Network Analyzer (VNA, RS-ZVB8, 300 kHz to 8 GHz) connects to one end of the transmission line test jig to generate a transverse electromagnetic (TEM) wave propagating along the transmission line and the other end of the test jig connects to the signal receiver (Port 2) of the VNA. With the given measurement setup, the forward transmission between Ports 1 and 2 (S_{21}) can be measured, with and without the presence of the material under test. With the measurement results, the SE of the sample can be determined as follows:

$$SE(dB) = S_{21,ref} - S_{21,load} \quad (3.5)$$

where $S_{21,ref}$ is the forward transmission measured with the reference specimen and $S_{21,load}$ is the insertion loss measured with the shield (load) specimen. Given the test jig's cross-sectional dimensions, the highest measurement frequency is limited to 1.2 GHz before the higher order propagation modes (i.e. non-TEM mode) become significant [137]. Therefore, the measurement will be carried out from 30 MHz to 1.2 GHz. The resolution bandwidth of the VNA is set at 100 kHz and 50 Ω coaxial cables are used to connect the ASTM test jig to the VNA.

Figure 3.1 Instrumental setup for measuring SE according to ASTM D4395-99.

3.3 Results and Discussion

3.3.1 FTIR spectroscopy

Figure 3.2 illustrates the interfacial reaction between the oxidized HCMs and the phenolic resin in the presence of glutaric dialdehyde. The hydroxyl functional group was generated on the surface of HCMs by oxidation in a strong nitric acid. The coupling agent, glutaric dialdehyde, used in this study has two functional aldehyde groups at both ends of the molecules. One aldehyde group can react with hydroxyl group which is on the surface of HCMs to form acetal linkage. Other aldehyde group will also react with phenolic resin

monomers and form hemiacetal linkage with resin matrix. The formation of acetal and hemiacetal linkages by the glutaric dialdehyde results in strong adhesion between HCMs and phenolic resin matrix.

Figure 3.2 Schematic process of chemical reaction between the oxidized HCMs and coupling agent.

FTIR spectra of Un-HCMs, oxidized HCMs, and CA-HCMs are illustrated in Figure 3.3. As shown in Figure 3.3 (b), the three bands at 3440 cm^{-1} , 1460 cm^{-1} , and 1084 cm^{-1} correspond to the O-H, C=C, and C-O stretching vibrations on surface of Un-HCMs, respectively. FTIR spectrum of the oxidized HCMs is presented in Figure 3.3 (a). It is found that the appearance of new peak of the vibration mode C-OH at 1384 cm^{-1} instead of the vibration mode C=C at 1460 cm^{-1} indicates that the C=C bond was broken during oxidation. In the meanwhile, the O-H peak at 3440 cm^{-1} slightly increases. The observation indicates that the surface of the HCMs has been functionalized by oxidation and hence the formation of -OH groups on the HCMs. Figure 3.3 (c) shows the FTIR spectrum of the CA-HCMs. It is observed that the -OH peak at 3440 cm^{-1} and 1384 cm^{-1}

decreases a little but C-O peak at 1084 cm^{-1} slightly shifts to 1156 cm^{-1} , which corresponds to the C-O-C vibration mode. This reveals that the coupling agent reacts with the -OH groups on the surface of the HCM to form acetal linkages. The remaining functional group on the coupling agent will react with the phenolic resin binder to form a cross-linking structure.

3.3.2 Effect of coupling agent on compressive properties

Figure 3.4 (a) and (b) show the stress-strain curves of compression tests of the syntactic foams containing various amounts of Un-HCMs and CA-HCMs, respectively. Similar compression studies of syntactic foams based on epoxy resin has also been previously discussed by other research groups [16, 138]. In general, for each individual curve, the compression stress-strain curves have three regions. Region 1 shows a linear increasing trend in compressive stress, which corresponds to the elastic behavior of the foam. This region ends when the syntactic foam reaches its compressive yield strength. At the end of the region 1, yielding and a slight decrease in strength occur, which is the characteristic of region 2. This region corresponds to the implosion of the HCMs. When a large number of microspheres get crushed and compacted, further increase in the load results in the densification of the foam and is visible as the region 3 of the curve.

Figure 3.3 FTIR spectra of hollow carbon microsphere: (a) oxidized HCMs, (b) Un-HC and (c) CA-HCMs.

The comparison of compressive yield strength as a function of HCMs content is shown in Figure 3.5. The compressive yield strength of syntactic foam containing the same volume fraction of hollow spheres increases due to the use of coupling agent treatment. It is noted that there are three main factors that affect the compressive yield strength when hollow spheres are added. The first factor is the introduction of more hollow space from the hollow spheres. These spaces take up large volume fraction of the composite, which reduces the compressive yield strength. The second factor is the bonding strength between the outer surfaces of the hollow spheres and the matrix. When the bonding strength is strong, the compressive yield strength is improved. The third factor is the influence of wall thickness-to-radius ratio, t/r , of hollow microspheres. The hollow microspheres with larger t/r can take up more load under compression [139]. In this study, only the first and second factor will be considered, as the Un-HCMs and CA-HCMs selected have the same t/r .

As shown in Figure 3.5, the compressive yield strength, σ_c , decreases with increasing filler content of Un-HCMs is observed. The decreasing trend indicates that when the hollow microsphere content is increased, the hollow space volume fraction also increases, which resulted in the decrease in compressive yield strength. It can also be seen that the compressive yield strength, σ_c , slightly increases upon inclusion of 9.4 vol% of CA-HCMs when compared to neat phenolic resin. However, beyond 9.4 vol%, a decrease in σ_c is observed. The upward trend is attributed to a relatively minor decrease in σ_c which results from the introduction of hollow space volume, compared to the increase in σ_c that results from the use of coupling agent. The decrease in σ_c with increasing CA-HCMs from 9.4 vol% to 46.9 vol% indicates that the reduction in strength which results from the introduction of more hollow space volume is larger than the relative increase in compressive yield strength that is attributed to the coupling agent treatment. It is also noted, from Figure 3.5, that the decrease in compressive yield strength for Un-HCMs with increasing filler content (from 9.4 to 46.9 vol%) is approximately 45.6%; whereas the decrease for the CA-HCMs samples is only 21.8%.

Figure 3.4 Compression stress-strain curves of the syntactic foams with various amounts of (a) Un-HCMs and (b) CA-HCMs.

The same trend is seen in Figure 3.4 (a) and (b). This is also attributed to the good interface adhesion between filler and matrix. When CA-HCMs are introduced, the interfacial strength between outer surfaces of HCMs and the phenolic resin increases.

These bonded interfaces will need to be overcome before the crushing of the microspheres and the occurrence of severe damage, which in turn improves the compressive yield strength. Nevertheless, on the other hand, when the hollow microspheres content increases, the more air space will decrease the absolute mass and reduce the compressive yield strength. The two effects overall result in a relatively little decrease in compressive yield strength for the CA-HCMs foams comparing with that for Un-HCMs foams, as filler is content increased.

Figure 3.5 Comparison of compressive strength as a function of HCMs content.

3.3.3 Effect of coupling agent on flexural properties

Figure 3.6 (a) and (b) show the flexural stress-strain curves for the syntactic foams containing various amounts of Un-HCMs and CA-HCMs, respectively. For all specimens, it is observed that both the strength and strain values are reduced with increasing filler content. The syntactic foams containing Un-HCMs are noted to show a larger reduction in

failure strain. The larger reduction in strain for Un-HCMs is also attributed to the poor interfacial adhesion between filler and binder. It is also noted that, from Figure 3.6 (a), the modulus (the slope of individual curve) of syntactic foam containing Un-HCMs decreases with increasing filler content. However, from Figure 3.6 (b), the modulus slightly increases upon inclusion of 9.4 vol% of CA-HCMs when compared to neat phenolic resin, whereas beyond 9.4 vol%, a decrease in modulus is observed. This is also attributed to the good interface adhesion between filler and matrix. This upward trend is also attributed to a relatively increase in modulus which results from the use of coupling agent, compared to minor decrease in modulus that results from the introduction of hollow space volume. The comparison of flexural strength as a function of HCMs content is illustrated in Figure 3.7. It is obvious that the flexural strength decreases with increasing filler content for both Un-HCMs and CA-HCMs samples. The decrease in flexural strength for Un-HCMs with increasing filler content (from 9.4 to 46.9 vol%) is approximately 56.3%; whereas the decrease for CA-HCMs is about 43.2%. The trend is also reflected in Figure 3.6 (a) and (b).

Figure 3.6 Flexure stress-strain curves of the syntactic foams containing various amounts of (a) HCMs and (b) CA-HCMs.

Luxmoore and Owen [140] suggested that an oversized void will initiate a crack when the foam is subjected to loading. After the crack propagates through the resin matrix, the resin matrix fails as a result of the failure of the foam. Figure 3.8 shows a fracture surface SEM image of the syntactic foam containing 28.1 vol% of CA-HCMs after flexure tests. The foam contains four constituent: HCMs, phenolic resin matrix, interface between microspheres and matrix and internal voids. The local phenomena include the crack initiating and passing through the internal void, the rupture of the microspheres-resin interface, the rupture of the microspheres and resin themselves. It could be seen that the crack initiates from an internal void which was formed during curing. When the crack is initiated, it will propagate to the phase that requires the lowest energy, or in other words, a phase that offers the least obstruction to the crack front propagation. Therefore, as seen in Figure 3.8, the crack propagates towards the nearest internal void. After the crack passing through the internal void, the crack grows through the interface between the microspheres and the resin, which results in the debonding of the microspheres and resin. For the syntactic foam containing CA-HCMs, good interfacial adhesion would hinder the progress of the crack at the interface and result in the final improvement of the overall strength. It is hence concluded that the main reason for the reduction in flexural strength when hollow spheres are added is the introduction of more voids, which is similar to the compression result discussed earlier.

Figure 3.7 Comparison of flexural strength as a function of hollow carbon microspheres content.

Figure 3.8 SEM micrograph of fracture surface of the syntactic foam after flexure tests.

3.3.4 Effect of coupling agent on fracture toughness

Figure 3.9 shows comparison of fracture toughness, K_{Ic} , of the foams with various HCMs contents. It is obvious that the fracture toughness of syntactic foams is improved by the use of coupling agent. As a general trend, fracture toughness increases up to 28.1 vol% and decreases beyond 28.1 vol% for both Un-HCMs and CA-HCMs. Such an optimal fracture toughness has been observed in different particulate composites [95, 96, 141]. The optimal fracture toughness suggests a change of dominant fracture mechanism. The syntactic foam containing CA-HCMs outperforming that containing Un-HCMs with a higher value of K_{Ic} has also suggested that the fracture toughness of syntactic foams could be improved by the use of coupling agent.

The various toughening mechanisms that may be operative in a syntactic foam are illustrated in Figure 3.10. The fracture toughness of syntactic foam could be influenced by a combination of crack deflection, crack bowing and debonding mechanism [142]. Figure 3.10 (a) shows crack deflection mechanism. Hollow microsphere, which acts as the reinforcing phase, perturbs the crack front propagation. Deflection results in a non-planar crack occurrence. Crack bowing mechanism, as shown in Figure 3.10 (b), is similar to crack deflection in that a non-linear crack front is caused due to the reinforcing phase hindering the progress of the crack. The stress intensity on the matrix is reduced by bowing while the reinforcing phase produced an increase in the stress intensity. When the stress intensity increases until fracture of the reinforcing phase, the crack continues to advance. Figure 3.10 (c) means that debonding occurs when the crack grows over the interface between microspheres and matrix. At this time, extra energy is required to break the adhesion force and create a new interface.

Figure 3.9 Comparison of fracture toughness of the foams with various contents of hollow carbon microspheres.

Figure 3.10 Schematic of proposed fracture mechanisms of the syntactic foams: (a) crack deflection mechanism, (b) crack bowing mechanism and (c) debonding mechanism.

Figure 3.9 shows that the use of CA-HCMs increases fracture toughness, which could be attributed to the debonding effect. Extra energy would be consumed to break the interfacial adhesion between microspheres and matrix when debonding occurs. Coupling agent creates good interfacial adhesion which needs more energy to break. When the syntactic foam contains the same amount of HCMs, good interfacial adhesion between filler and matrix would result in the higher fracture toughness.

Figure 3.11 shows SEM micrographs of fracture surface of the syntactic foams containing 9.4 vol% Un-HCMs and CA-HCMs, respectively. In Figure 3.11 (a), it can be seen clearly that both fully and partially debonded microspheres are present in the matrix. There are gaps around the debonded microspheres, which results from the plastic dilatation of the matrix when debonding occurs [95]. As discussed earlier, the crack needs extra energy to break the interfacial adhesion and create a new interface as it reaches the interface between microspheres and matrix. The microspheres would be easily debonded as long as the interfacial adhesion is poor. Therefore, in Figure 3.11 (a), the number of debonded microspheres is larger than that of deformed microspheres. On the other hand, the crack may propagate through the microspheres before the interfacial adhesion is broken as long as the interfacial adhesion is strong. This leads to fracture of the microspheres. As a result, compared to Figure 3.11 (a), Figure 3.11 (b) reflects the opposite. It can be seen that more deformed microspheres are present, which is ascribed to the strong interfacial adhesion. Similar phenomena can also be observed more clearly in Figure 3.12, which shows the fracture surface of the syntactic foam containing high volume fraction of Un-HCMs and CA-HCMs.

Besides the debonded microspheres, it is noted that samples with lower microsphere contents have larger inter-particle separation between microspheres and non-planar and non-linear cracks in the fractured surface in Figure 3.11. These cracks are likely resulted from the debonding and fracturing of microspheres. They can be used as

an evidence of the existence of a combination of crack deflection and bowing mechanisms. However, it can be seen from Figure 3.12, that the inter-particle separation between microspheres decreases as the volume fraction of microspheres increases, which decreases the effect of crack deflection mechanism. Under these circumstances, the premature cracks would be blocked by the neighbor microspheres and could not propagate further. Most energy will concentrate to break the interfacial force and results in the debonded and fractured of microspheres. Therefore, we reckoned that the increase in K_{Ic} for 0-28.1 vol% filler content is attributed the combination of crack deflection and bowing mechanisms. The decrease in K_{Ic} beyond 28.1 vol% of filler content suggests the dominate mechanism has changed to the combination of crack bowing and debonding mechanisms.

Figure 3.11 SEM micrograph of fracture surface of the syntactic foam containing 9.4 vol% Un-HCMs (a) and CA-HCMs (b) after fracture toughness tests.

Figure 3.12 SEM micrograph of fracture surface of the syntactic foam containing 46.9 vol% Un-HCMs (a) and CA-HCMs (b) after fracture toughness tests.

3.3.5 Effect of coupling agent on SE

Due to the highest fracture toughness obtained at 28.1 vol% of filler content, the amount of filler was fixed at 28.1 vol% for EMI SE tests. Table 3.1 lists EMI SE values of the syntactic foams containing Un-HCMs and CA-HCM. The mean and standard deviations of SE were calculated based on 201 data points in the frequency range 30 MHz to 1.2 GHz.

It has been discussed earlier (in Section 2.6) that EMI shielding performance of a material is highly related to the electrical conductivity of the materials. The phenolic resin is almost transparent to EM wave because it is an insulator. It can be seen from Table 3.1 that after the introduction of HCMs, SE value of the syntactic foam reaches approximately 1.7 dB. According to the definition of SE (equation 2.1), 1.7 dB means that the material can shield only 32.4% of the incident EM radiation. The EMI shielding performance of a composite material depends on many factors, such as the filler's aspect ratio and intrinsic conductivity [127, 128]. Compared with tube-like fillers, in this study, the spherical HCMs have lower aspect ratio. For the syntactic foam containing

approximately 28 vol% of HCMs, very little HCMs connect with one another, hence, a conductive network is not formed (see Figure 3.8). Besides the aspect ratio, low SE value of the syntactic foam implies that HCMs possess low intrinsic electrical conductivity. The overall effect of the two factors caused the poor EMI shielding performance of the syntactic foam. Literatures showed that the use of coupling agent could improve the dispersion of carbon fiber and carbon nanotube (CNT) filler and hence result in the enhancement in EMI SE [122, 124]. However, our EMI test results show that the SE of the syntactic foam containing CA-HCMs is almost the same as that of the syntactic foam containing Un-HCMs. This means that the coupling agent has no effect on EMI performance of the syntactic foam. The likely reason is that due to the low volume fraction and small aspect ratio of HCMs, no agglomeration of HCMs was observed no matter whether a coupling agent was introduced. Therefore, although the introduction of coupling agent can improve the interfacial adhesion between HCMs and phenolic resin, electrical conductive network is not formed.

Table 3.1 The comparison of EMI SE value (frequency range from 30 MHz to 1.2 GHz).

Sample	EMI SE (dB)
	$\bar{x} \pm z$
Un-HCMs syntactic foam	1.68 ± 0.51
CA-HCMs syntactic foam	1.72 ± 0.59

3.4 Concluding remarks

(1). HCMs could be treated by using coupling agent, through the chemical reaction process involving the oxidization of HCMs followed by the treatment with a coupling agent of glutaric dialdehyde.

(2). It was demonstrated that compressive and flexure strengths decreased with increasing volume fraction of HCMs. The mechanical properties of the syntactic foam containing CA-HCMs were better than those of the syntactic foam containing Un-HCMs, because coupling agent facilitated better adhesion of the HCMs to the matrix.

(3). It was also found that the highest fracture toughness values were observed in the samples with 28 vol% of filler and the fracture toughness increased by the use of coupling agent.

(4). The dominant toughening mechanism changed from the combination of crack deflection and bowing to the combination of crack bowing and debonding mechanisms beyond 28 vol% of filler content.

(5). 1.7 dB of SE was obtained for syntactic foam containing approximately 28 vol% of HCMs. The poor EMI performance of the syntactic foam was attributed to the low aspect ratio and intrinsic electrical conductivity of HCMs.

(6). The use of coupling agent had no effect on EMI performance of the syntactic foam, because no electrical network was formed in the matrix.

Chapter 4. Effect of carbonization on mechanical properties and EMI shielding performance of syntactic foams

4.1 Introduction

It has been studied in Chapter 3 that syntactic foam containing HCMs exhibits negligible SE due to the insulating nature of the matrix and the fact that no electrical network is formed. The introduction of the coupling agent improved mechanical properties of the syntactic foams but it had no effect on their EMI shielding performance. The poor SE performance of the syntactic foam containing HCMs limits its practical application in EMI shielding. Therefore, the objective of the Chapter is to develop syntactic foams with EMI shielding performance.

Besides modifying the conductive microspheres, enhancing conductivity of the matrix is another approach to obtain desirable EMI shielding performance of syntactic foams. As reviewed in Section 2.7.2, carbon matrix is superior in EMI shielding compared to polymer matrices. However, developing conductive syntactic foams by carbonization has not been reported. Therefore, in this work, a processing method for carbonization of the phenolic matrix was developed. The syntactic foam was first prepared by adding HCMs into phenolic resin, followed by post-curing, pre-carbonization and carbonization. The effects of heat-treatment on the EMI SE and mechanical properties of the syntactic foam were studied. Mechanical properties studied included compressive and flexural strengths. The underlying mechanisms for failure behavior of the foams as well as improved electrical conductivity and SE properties will also be discussed in this chapter. It is expected that the mechanical properties will be decreased,

while the conductivity will be increased after the carbonation because the phenolic resin matrix will be converted to glassy carbon [143]. Therefore, the carbonization approach would be beneficial for special application where EMI shielding is critical and mechanical properties are not essential.

4.2 Materials and experimental procedures

4.2.1 Raw materials

Two basic materials, HCMs and a high carbon yield phenolic resin, were used to prepare the syntactic foam. The details have been described in Section 3.2.1.

4.2.2 Preparation of syntactic carbon foam

Preparation of the syntactic foams containing HCMs has been described in Chapter 3. After preparation of the syntactic foam, heat-treatment process was followed, played a significant role in forming carbon matrix. In this study, the syntactic foam was post-cured in a convection oven with circulated air (heated to a temperature of 200 °C) for a period of 32 hours. The specimens were then cooled to room temperature at 3 °C/min. After post-curing, the samples were pre-carbonized through two steps. Firstly, the post-cured samples were heated to 400 °C and dwelt for 3 h in argon atmosphere and then cooled to room temperature at 3 °C/min. Secondly, the samples were heated to 600 °C and dwelt for 3 h in argon atmosphere and cooled to room temperature at 3 °C/min. After pre-carbonization, the specimens were heated at 900 °C under a continuous purge of argon. The heating rate was maintained at 0.5 °C /min in order to minimize the formation of shrinkage, cracks, and slit pores, which could be caused by thermal expansion mismatch between the HCMs and the phenolic resin matrix. Figure 4.1 illustrates the process. The samples were heated at 25 °C, 200 °C, 400 °C, 600 °C and

900 °C in order to study the effects of heating temperature. These samples were labeled as C25, C200, C400, C600 and C900.

Figure 4.1 Flowchart of processing of the syntactic carbon foams.

4.2.3 Mechanical and EMI SE measurements

Mechanical tests in this chapter involve compressive and flexural strengths. The experimental procedures of mechanical tests and EMI SE measurement have been described in Section 3.2.5 and 3.2.6.

4.2.4 Electrical conductivity measurements

A four probe technique was used to measure the electrical conductivity of specimens. Both sides of the samples were measured and the measured conductivity values were then averaged. All the results were the average of five tests.

The classical formula of a thick bulk material can be expressed as:

$$\sigma = \frac{1}{R} = \frac{I}{2\pi S \times V} \quad (4.1)$$

where σ is the electrical conductivity (S/cm), R is the resistivity ($\Omega \cdot \text{cm}$), S is the probe spacing (cm), V is the measured voltage (V) and I is the source current (A).

4.2.5 Raman spectroscopy measurements

To study the carbon structure in matrix after carbonization of the syntactic foams, Raman spectra were recorded by using a WITEC CRM200 system with spectral resolution of 1 cm^{-1} . In order to avoid thermal effect of laser, the laser power was kept below 0.5 mW and the excitation laser was 532 nm (2.33 eV). A $100 \times$ objective lens with a numerical aperture of 0.95 was used.

4.2.6 Microstructural characterization

Microstructures of the syntactic carbon foams were examined by using a Jeol JSM 6360 SEM.

4.3 Results and discussion

4.3.1 Shrinkage and weight loss

Figure 4.2 shows weight loss and volume shrinkage of a typical specimen after different heat-treatment processes. The properties of the syntactic foam could be dominated by the phenolic resin matrix due to the earlier heat-treatment of HCMs. The

syntactic foam was converted into a black carbonaceous mass accompanied by the weight loss and volume shrinkage during pyrolysis from room temperature to 900 °C. The weight loss took place in two steps, while the volume shrinkage was achieved in one step. In the first step, the weight loss took place during the post-curing stage and was attributed to the phenolic resin. This process promoted the cross-linking and condensation reactions and led to the formation of long-chain, cross-linked polymeric structures in the matrix [144]. At the end of this stage, the matrix was still polymeric. In the first pre-carbonization stage between 200 °C and 400 °C, the weight loss and volume shrinkage of the composites were not very significant. More weight loss and greater volume shrinkage occurred during the second pre-carbonization between 400 °C and 600 °C. This was attributed to the loss of volatile components and other organic compounds. In the second pre-carbonization stage, the matrix was converted to carbon. At the end of the pre-carbonization stage, the carbon to hydrogen ratio was 2:1. The remaining hydrogen was successively removed in the following carbonization stage, which was accompanied by the slight change of weight loss and volume shrinkage. After carbonization, the linearly conjugated carbon domains were interlinked, resulting in a continuous turbostratic carbon structure [145]. The volume shrinkage of the composites was approximately 34% and was accompanied by a weight loss of 49%, which resulted in the low density of syntactic carbon foam. The relationship between properties and heat-treatment stage will be discussed later.

Figure 4.2 Typical volume shrinkage (%) and weight loss (%) of the samples after being treated at different temperature.

4.3.2 Microstructure of the syntactic carbon foam

Figure 4.3 shows microstructure of sample C900. The foam has three constituents: carbon matrix, HCMs and internal voids. It could be seen that very little HCMs connected with one another and most of HCMs remained substantially unbroken. A good interconnected network was formed through the matrix. The formation of network in the matrix could result in high electrical conductivity and good EMI SE, which will be discussed in detail in the following section.

Figure 4.3 Microstructure of the sample C900.

4.3.3 Effects of temperature on electrical conductivity

Table 4.1 lists electrical conductivities of the samples measured at room temperature. It can be seen that the electrical conductivity kept nearly constant from C25 to C600. The formation of an electrical network within in the matrix plays a key role in the electrical conductivity of the specimen. The low electrical conductivity of the samples from C25 to C600 is due to the non-conductive nature of the phenolic resin. The incomplete carbonization is responsible for the low carbon content in the matrix. An increase in conductivity by approximately seven orders of magnitude was obtained for the sample C900 after complete carbonization. For the sample C600, the carbon content is still not sufficiently high to form a good interconnected network. Chhowala et al. [146] suggested that the content of sp^2 hybridization in the carbon materials predominantly promoted electronic and transport properties. Figure 4.4 shows a typical spectrum, characterized by two main peaks centred at 1350 and 1587 cm^{-1} , respectively. It was observed that both sp^3 and sp^2 signals of C900 were much stronger than those of C600. In

Figure 4.4, when comparing the line (B), which corresponds to sp^3 -rich carbon, C600, and the line (A), which corresponds to an increased sp^2 -banded carbon, C900, it is noted that the higher sp^2 content of C900 led to its high electrical conductivity. The electrical conductivity increased from 1.33×10^{-7} to 1.20 S/cm.

Table 4.1 Electrical conductivity at room temperature for different samples.

Sample	Room temperature conductivity (S/cm)
C25	1.33×10^{-7}
C200	1.35×10^{-7}
C400	1.38×10^{-7}
C600	1.36×10^{-7}
C900	1.20

Figure 4.4 Typical Raman spectrums of C600 (B) and C900 (A).

4.3.4 Effect of carbonization on SE

Table 4.2 compares EMI SE of C25 with that of C900. The measured SE for the various samples was observed to be generally frequency independent with slight deviation. The mean and standard deviation of SE over 201 data points in the frequency range 30 MHz to 1.2 GHz were calculated and shown in Table 4.2. It has been discussed earlier (Section 2.6) that the EMI shielding performance is highly related to the electrical conductivity of the materials. Based on the data obtained from Tables 4.1 and 4.2, it is obvious that there is a strong correlation between electrical conductivity of the foam and its associated SE. From the table, it can be observed that SE of C900 is better than that of syntactic foam by a factor of 16, while electrical conductivity is increased by approximately seven orders of magnitude. The increase in electrical conductivity in C900 was due to the sufficient amount of sp^2 in the carbon matrix after carbonization. The presence of sp^2 after carbonization increased the interconnected electrical network within the matrix leading to higher SE. The SE of C900 reached 30.48 dB, which means C900 can shield 99.91% of the incident EM radiation according to the definition of SE (Eq. 2.1). Because of some advanced applications related to EMI shielding, the specific EMI SE is more appropriate for use in comparing the shielding performance between typical metal-based and conducting polymer composites materials. Specific EMI SE is defined as the SE per unit density of the material. In this work, the specific EMI SE of C900 was calculated to be $34.29 \text{ dB}\cdot\text{cm}^3/\text{g}$, which is much higher than that of copper ($10 \text{ dB}\cdot\text{cm}^3/\text{g}$) and 43 vol% 20 μm Ni fibers/PES composites ($16 \text{ dB}\cdot\text{cm}^3/\text{g}$) [147].

Table 4.2 EMI SE values (frequency range from 30 MHz to 1.2 GHz).

Sample	EMI SE (dB)
	$\bar{x} \pm z$
C25	1.68 ± 0.51
C900	30.48 ± 1.79

With the transmission line test jig setup, through the scattering parameter (S-parameter), the reflectance (R), absorbance (A) and transmittance (T) of the incident EM wave propagating through the shield sample can be determined as follows:

$$R = \left| \frac{P_R}{P_I} \right|^2 = |S_{11}|^2 = |S_{22}|^2 \quad (4.2)$$

$$T = \left| \frac{P_T}{P_I} \right|^2 = |S_{12}|^2 = |S_{21}|^2 \quad (4.3)$$

$$A = 1 - R - T \quad (4.4)$$

where P_R , P_T , and P_I refer to reflected, transmitted and incident powers; respectively; and S_{11} , S_{22} , S_{21} , and S_{12} are input reflection, output reflection, forward transmission, and reverse transmission, respectively. It has been reported that the SE of a material can be determined by the ratio of transmitted power in the absence of the shield to the transmitted power in the presence of the shield. Expressing in dB, it can be expended into three terms as follows [148]:

$$SE_{overall} = SE_R + SE_A + SE_{MR} (dB) \quad (4.5)$$

where SE_R is the reflection loss caused by reflection of the wave at the first boundary, SE_A is the absorption loss of the wave when it propagates through the shield and SE_{MR} accounts for the effect caused by multiple-reflections between the first (air-material) and second (material-air) boundaries. (refer to Figure 2.13) Typically, the magnitude of EM wave decreases exponentially as it penetrates a conductive material, which is best quantified in terms of skin depth. The depth at which the magnitude of EM wave decays to $(1/e)$ of the incident wave is referred to as one skin depth (δ), which is related to the

electrical properties of the material. If the shield is thicker than one skin depth, the effect of multiple reflections can be ignored [107].

$$\delta = (\pi f \sigma \mu)^{-1/2} \quad (4.6)$$

where f is frequency (Hz), $\mu = \mu_0 \mu_r$, μ_r is the relative permeability of the material and $\mu_0 = 4\pi \times 10^{-7}$ is the absolute permeability of free space (H/m) and σ is the electrical conductivity of the material (S/m). For C900, since it can be considered as a non-magnetic substance, we can assume $\mu_r = 1$. The effect of multiple reflections that affect the overall SE can be calculated by [108]:

$$SE_{MR} = 20 \log |1 - e^{-2/\delta}| \quad (4.7)$$

Table 4.3 shows the calculated skin depth value and SE_{MR} of C900 at three different fixed frequencies. In this work, the thickness of the specimen was kept at 3 mm. According to calculations, the effect of multiple-reflections can be ignored at high frequency as the skin depth becomes smaller. Hence, Eq. (4.5) can be simplified as:

$$SE_{overall} = SE_R + SE_A \quad (4.8)$$

However, the effect of multiple-reflections cannot be neglected at lower frequency range. Equation (4.7) shows that the SE_{MR} is a negative term, which leads to reduction of the overall SE of the material. Based on the definitions of EMI SE and the Eqs. (4.2) and (4.3), $SE_{overall}$, SE_R , and SE_A can be mathematically interpreted as follows:

$$SE_{total} = -10 \log T \quad (4.9)$$

$$SE_R = -10 \log(1 - R) \quad (4.10)$$

$$SE_A = SE_{total} - SE_R - SE_{MR} \quad (4.11)$$

Table 4.3 also lists the contributions of reflection, absorption and multiple-reflections to the overall EMI SE of C900 at three different fixed frequencies according to the equations (4.9)-(4.11). It is obvious that wave reflection was the major contribution of SE . For the C900 at 700 MHz, shielding by reflection was approximately 78% of the overall SE . This

means that when the EM wave encountered the specimen, the energy reflected was higher than that being absorbed. Based on these observations, it became clear that most of the attenuation of the C900 was due to reflection.

Table 4.3 Skin depth and the contribution of reflection, absorption and multiple-reflections in the overall SE of C900 at different fixed frequency.

Frequency (MHz)	Skin depth (mm)	SE_R (dB)	SE_A (dB)	SE_{MR} (dB)
400	7.77	26.72	9.14	-5.38
700	5.87	24.28	10.09	-3.89
1200	1.42	21.92	8.56	Neglect

4.3.5 Effects of temperature on compressive and flexural properties

Figure 4.5 shows compressive and flexural strengths of the foams after being treated at different temperatures. It can be seen that flexural strength increased after the sample was post-cured. The post-curing treatment led to the formation of good cross-linking polymeric structures in the matrix. After post-curing, the flexural strength decreased sharply for C400, which corresponds to the decomposition of resin matrix. After the first pre-carbonization stage, the flexural strength decreased slightly and then kept nearly constant between the second pre-carbonization and final carbonization stage. The specimen showed brittle behavior as the phenolic resin after pre-carbonization treatment was converted to glassy carbon. Similar trends were observed in compressive strength, as shown in Figure 4.5. In Chapter 3 and 4, the typical compression stress-strain

curve of syntactic foam has been described and discussed. It is divided into three distinct regions: elastic deformation, densification region and densification completed [15]. Interestingly, in this study, the stress-strain curves of C25 and C200 also showed three similar regions. However, after post-curing stage, the stress-strain curve of compressive tests becomes different. Figure 4.6 illustrates compression stress-strain curve of C200, which has typical three regions. This means that the matrix is still polymeric. Figure 4.7 shows stress-strain curve of C600. Only region 1, which corresponds to the elastic deformation region, was observed. The formation of the brittle carbon matrix led to the much lower strength and strain. At the end of this region, the matrix was crushed as a result of failure of the material. Here, it is worth noting that fracture toughness tests were not carried out on the carbonized foams due to the brittleness of the specimen after heat-treatment.

Figure 4.5 Compressive and flexural strengths of treated samples.

Figure 4.6 Compression stress-strain curve of C200.

Figure 4.7 Compression stress-strain curve of C600.

4.4 Concluding remarks

(1). Syntactic foam with carbon matrix could be achieved by thermal treatment of syntactic foam with phenolic resin. The process consisted of post-curing, pre-carbonization and carbonization.

(2). After carbonization, the composites experienced on approximately 34% volume shrinkage and 49% weight loss, resulting in a decrease in their density.

(3). After carbonization, electrical conductivity of the syntactic foam, measured at room temperature, was increased by approximately seven orders of magnitude. SE of the syntactic foams after carbonization were higher than those without carbonization by a factor of 16. The formation of sp^2 hybridization after carbonization facilitated the formation of an increased electrical network within the matrix that led to higher SE. The SE value of 30 dB means that the material can shield over 99.91% of the incident EM radiation.

(4). It was found that shielding by reflection was the dominant mechanism. It was also found that multiple-reflections have a negative contribution to the overall SE at relatively low frequencies when the shield thickness was smaller than the skin depth. On the contrary, the effect of multiple-reflections can be ignored at high frequency.

(5). It was also found that mechanical properties of the syntactic foams, such as compressive and flexure strengths, were strongly dependent on the heat-treatment temperature. The compressive and flexural strengths were improved after the post-curing stage and then decreased after pre-carbonization and final carbonization stages. The increase could be due to the formation of long-chain, good cross-linking polymeric structures in the matrix. The decrease was resulted from the introduction of more interval voids and the formation of glassy carbon caused by the heat-treatment.

Chapter 5. CNFs reinforcement on mechanical properties and EMI shielding performance of syntactic foams

5.1 Introduction

The approach studied in Chapter 3 demonstrated that the introduction of the coupling agent facilitated chemical bonding between the matrix and the microspheres, hence improving mechanical properties of the syntactic foams. However, the coupling agent approach didn't provide with EMI shielding function of the syntactic foam. This is because the coupling agent has not able to form electrical network and HCMs had low intrinsic conductivity. On the other hand, as demonstrated in Chapter 4, after fully carbonization, electrical conductivity of the syntactic foam was increased by approximately seven orders of magnitude and consequently its SE was enhanced by a factor of 16. This is because the carbon matrix is electrically conductive. However, it is also noted that mechanical properties of the syntactic foam decreased after fully carbonization. The poorer mechanical properties were ascribed to the introduction of more interval voids and glassy carbon after carbonization. Based on findings and insights, it is reckoned that an approach which can increase mechanical properties while maintaining EMI shielding performance of the syntactic foams will be of great interest.

5.2 Materials and experimental procedures

5.2.1 Raw materials

Two basic materials, HCMs and a high carbon yield phenolic resin, were used to prepare the syntactic foams. Details have been described in Section 3.2.1. The CNFs used

for reinforcement of the syntactic foam were Pyrograf®-III supplied by Applied Sciences, Inc, OH, USA. The fiber diameters vary from 60 nm to 150 nm, and the density is 1.95 g/cm³.

5.2.2 Preparation of carbon nanofiber reinforcement syntactic foams (CNFRSFs)

Fiber volume fractions were 0.5, 1.0, 1.5 and 2.0 vol%. The resin was heated to 50 °C to reduce its viscosity before adding the CNFs. The mixture was then stirred by high-shear homogenizer (Sliverson L4R) at 4500 rpm for 30 minutes to obtain uniform dispersion of CNFs. A stoichiometric quantity of hardener was then added and stirred in the mixture. The beaker containing the mixture was submerged in an ice-bath in order to avoid a temperature rise during the stirring process. After well dispersed CNFs were attained, a weighed quantity of HCMs was added in multiple steps to the mixture. The amount of HCMs was fixed at around 28 vol% as this ratio has been shown to have the highest fracture toughness of the syntactic foam in the previous work. The processing route of fiber-first-HCMs-second was applied in order to avoid a situation where a greater number of regions display accumulated voids [104]. After the addition of HCMs, the mixture was molded using an aluminum mold coated with a silicone release agent and left under a constant pressure of 2.0 MPa for 24 hours to cure at room temperature.

5.2.3 Preparation of CNF composites

To compare SE values between CNFRSFs and CNF composites, the addition of the CNF volume fraction to the phenolic resin of CNFRSF was the same as that to the phenolic resin of CNF composites. Based on the calculation, 0.7, 1.4, 2.1 and 2.8 vol% of CNFs were added to the phenolic resin. The dispersion process was similar with that of preparation of the CNFRSF. After dispersion, the mixture was molded using an aluminum

mold coated with a silicone release agent and left under a constant pressure of 2.0 MPa for 24 hours to cure at room temperature.

5.2.4 Mechanical and EMI SE tests

Mechanical tests in this chapter involve compressive and flexural strengths. The experimental procedures of the mechanical tests and EMI SE measurement were described in Section 3.2.5 and 3.2.6.

5.2.5 Electrical conductivity measurements

The electrical conductivities of the specimens were measured using a four probe technique. The conductivity was measured on both sides of each specimen and then averaged. All the results were an average of five tests.

5.2.6 Microstructural characterization

Fracture surface of the samples was examined by using a Jeol JSM 6360 SEM. It is worth noting that compressive failure image was taken in the densification region (region 2).

5.3 Results and discussion

5.3.1 Effect of CNFs reinforcement on compressive property

Figure 5.1 shows compressive yield strengths of the CNFRSF as a function of CNFs content. The error bar is the standard deviation for five measured values. It is obvious that the compressive strength of CNFRSF remains nearly constant with increasing CNFs content. Figure 5.2 shows stress-strain curve of the CNFRSF containing 1.5 vol% CNFs. The stress-strain curve is divided into three distinct regions: elastic

deformation (region 1), densification region (region 2) and densification completed (region 3) [15]. In order to determine the structure-property relationship, the specimens were examined in a SEM before the stress-strain curve reaches region 3. Figure 5.3 shows compressive failure feature of the CNFRSF containing 1.5 vol% CNFs in region 2 of the stress-strain curve. It is obvious that all microspheres are crushed in this region. As discussed earlier, an oversized void would initiate a crack when a composite is subjected to loading [140]. Under compressive loading conditions, the microspheres were crushed. The crushing of the microsphere leaves oversized voids and debris in the matrix, which behaves as the initiation of the crack. Upon the compressive yielding, most of the microspheres were crushed and resulted in severe damage occurrence. It can also be seen in Figure 5.3 that most of the CNFs are uniformly embedded and well separated in the matrix when the compressive strength reaches in the range of region 2. Only a few pulled-out and debonding CNFs are observed. This meant that the failure of the specimen is dominated by the microspheres crushing, while CNFs and the matrix play smaller roles in this case. Compared with CNFs reinforced resin area, the phase of HCMs is weaker and more brittle. The failure of the sample originates from the weaker phase in the syntactic foam. In other words, the presence of microspheres in the CNFRSF is the primary load bearing phase in the hybrid composite when the specimen is subjected to compressive loading. Hence, the presence of CNFs does not lead to any enhancement in the compressive strength of the CNFRSF.

Figure 5.1 Compressive yield strength of the CNFRSF containing various amounts of CNFs.

Figure 5.2 Compression stress- strain curve of the CNFRSF containing 1.5 vol% CNFs.

Figure 5.3 Compressive failure feature of the CNFRSF containing 1.5 vol% CNFs in the region 2 of the stress-strain curve.

5.3.2 Effect of CNFs reinforcement on flexural property

Figure 5.4 shows flexural strength of the CNFRSF containing various amounts of CNFs. The error bar is the standard deviation for five measured values. It is observed that the flexural strength increases approximately by 196% as the CNFs filler content is increased from 0 to 1.5 vol%. Although a 10% decrease is observed from 1.5 to 2.0 vol%, the flexural strength of the CNFRSF increases approximately by 1.77 times compared to the CNFs-free syntactic foam. The increase in strength is attributed to the increase in load bearing of the fibrous reinforcements. On the other hand, the decrease in strength of the CNFRSF containing 2.0 vol% CNFs compared to that of the CNFRSF containing 1.5 vol% CNFs is ascribed to the stress concentration resulting from the agglomeration of the CNFs. At higher concentrations, CNFs may tangle and produce agglomeration because of their

high aspect ratio and van der Waals attractive interactions. The decreasing trend due to the agglomeration of CNFs together with the fracture toughness properties will be discussed in detail later.

As discussed earlier, Luxmoore and Owen [140] suggested that the failure of the matrix causes the failure of the foam. Figures 5.5 and 5.6 show SEM micrographs of the fracture surface of the CNFRSF containing 0.5 vol% CNFs after flexural tests with low and high magnifications, respectively. As seen in Figure 5.5, it is observed that the process under flexural loading involves microsphere debonding, microsphere fracture and deforming rather than the crushing of microspheres. Although deformed microspheres are present, their amount is much smaller than that of debonded and fractured microspheres. This is ascribed to the fact that the microspheres in the CNFRSF are not the primary load bearing phase under flexural loading. The failure of the specimen is dominated by matrix fracture. This observation is dissimilar to the condition under compressive loading. Figure 5.6 confirms the random orientations of CNFs on the fracture surface. It is clearly seen that the matrix around CNFs shows increased deformation compared to areas without CNFs. The pulled-out and debonding of CNFs are also observed in Figure 5.6, resulting in the formation of non-linear and non-planar micro-cracks. These micro-cracks are considered as additional tiny step structures that consume more bending energy. Phenolic resin suffices wet CNFs when the specimen contains low volume fraction of CNFs, leading to effective load transfer from matrix to CNFs. Therefore, it is concluded that the CNFs and the matrix are likely to be the primary load bearing phases under flexural loading.

Figure 5.4 Flexural strength of the CNFRSF containing various amount of CNFs.

Figure 5.5 SEM micrograph of fracture surface of the CNFRSF containing 0.5 vol% CNFs after flexural tests (low magnification).

Figure 5.6 SEM micrograph of fracture surface of the CNFRSF containing 0.5 vol% CNFs after flexural tests (high magnification).

5.3.3 Effect of CNFs reinforcement on fracture toughness

Figure 5.7 shows fracture toughness of the CNFRSF containing various amount of CNFs. The error bar is the standard deviation for five measured values. It can be seen that the fracture toughness, K_{Ic} , increases with the addition of 1.5 vol% of CNFs, and decreases beyond 1.5 vol% of CNFs. K_{Ic} increases from $2.19 \text{ MPa}\cdot\text{m}^{0.5}$ for CNFs-free syntactic foam to $3.01 \text{ MPa}\cdot\text{m}^{0.5}$ for CNFRSF containing 1.5 vol% CNFs, i.e. an increase of about 37.4%.

Figure 5.8 shows SEM micrograph of fracture surface of the CNFs-free syntactic foam after fracture toughness tests. The toughening mechanism of fiber-free syntactic foam was discussed in Chapter 3. Here, the mechanisms are described briefly. It is clearly seen that the step structures prevail for the microstructures of syntactic foam. A crack propagates through the matrix when the specimen is subjected to loading. As the crack reaches the interface between microsphere and matrix, it would be pinned by the rigid

microsphere and consequently break away from the rigid microsphere. A step structure would be formed when the crack propagates at different crack planes. These step structures are considered as new surfaces that consume fracture energy. As a result, the crack front bowing mechanism is considered as the main toughening mechanism. Figure 5.9 shows SEM micrograph of the fracture surface of syntactic foam containing 2.0 vol% CNFs after fracture toughness tests. Compared with Figure 5.8, CNFRSF containing high volume fraction of CNFs displays rougher fracture surface. The rougher surface implies that the propagation of the crack was distorted because of the presence of CNFs, making it more difficult. The inset image with high magnification in Figure 5.9 clearly shows the deformation of the matrix and the pulled-out CNFs. The fiber pullout results from debonding of the CNFs from the matrix. This causes fibers to bridge cracks.

It is also noted that the step structure is not observed in Figure 5.9 (compared to Figures 5.5 and 5.8). This suggests a change in the dominant fracture mechanism. The step structures occurring in CNFRSF containing low volume fraction CNFs are caused not only by the micro-cracks which results from the addition of CNFs, but also by the deformation of the matrix where there is no CNFs. At low volume fraction of CNFs, the area of matrix without CNFs is much larger than that reinforced by CNFs. Therefore, the step structure is mainly due to the fracture of the matrix itself. With the addition of more CNFs, nanofibers are more uniformly distributed and embedded in the overall resin matrix and this enhances the matrix property. When the cracks propagate along the matrix, micro-cracks prevail and make the propagation more difficult. Thus, the overall fracture toughness is improved. Figure 5.10 shows clusters and agglomeration of CNFs on fracture surface of the CNFRSF containing 2.0 vol% CNFs. The clustering and agglomeration of CNFs may act as pre-existing micro-cracks within the matrix and caused the reduction in fracture toughness. From Figure 5.10, it can also be seen that the CNFs are not completely wet by the resin matrix. Hence, the CNFs are less effective in

bearing the load that was transferred from the matrix. In addition, the incomplete wetting of CNFs by the resin could make the interfaces between CNFs and the matrix to be filled with some air and behave as open porosities, thus reducing the fracture toughness.

Figure 5.7 Fracture toughness of CNFRSF containing various amount of CNFs.

Figure 5.8 SEM micrograph of fracture surface of the CNFs-free syntactic foam after fracture toughness tests.

Figure 5.9 SEM micrograph of fracture surface of the syntactic foam containing 2.0 vol% CNFs after fracture toughness tests.

Figure 5.10 SEM micrograph of fracture surface of the CNFRSF containing 2.0 vol% CNFs after fracture toughness tests.

5.3.4 Effect of CNFs reinforcement on SE

Figure 5.11 shows measured SE over 30 MHz – 1.2 GHz for the CNFRSF with various amounts of CNFs. It is clearly observed that there is a strong correlation between concentration of CNFs and better SE. The highest SE obtained is found to be 25 dB at 1.2 GHz for the composite with 2.0 vol% CNFs loading. According to the definition of SE (Eq 2.1), a SE value of 25 dB meant that the material can shield more than 99.68% of the incident electromagnetic radiation. In general, 20 dB of SE is adequate for most practical applications. Therefore, the composite with 2.0 vol% CNFs loading is able to meet commercial EMI shielding specifications, such as mobile phone casing [149]. Using 1.2 GHz SE measurement results for comparison purpose, Figure 5.12 illustrates the relationships between CNFs content, electrical conductivity and SE. The results showed that by increasing the CNFs content in the foam composite, better electrical conductivity and higher SE were obtained. The increase in electrical conductivity is attributed to the formation of an electrical network. With increasing in CNFs loading, CNFs can easily interconnect with each other in the foam composite and lead to higher electrical conductivity. It is also noted from Figure 5.11, that the EMI shielding performance of CNFs-free syntactic foam (0 vol %) is very poor. As discussed earlier in Section 2.7.3, the SE of a composite material depends on many factors, such as the filler's aspect ratio and intrinsic conductivity [127, 128]. Compared to nano-scaled CNFs, micro-scaled HCMs possesses relatively lower aspect ratio and shows poorer connectivity between adjacent HCMs conductive units. For CNFs-free syntactic foam, the low intrinsic conductivity of HCMs results in the poor SE of the syntactic foam. It can hence be concluded that the conduction of the composite is highly influenced by the electrical connectivity network and the intrinsic conductivity of the filler.

Figure 5.11 EMI shielding effectiveness as a function of frequency for the CNFRSF with various CNFs content.

Figure 5.12 Relationships among CNFs content, electrical conductivity and EMI SE of the samples at 1.2 GHz.

Figure 5.13 illustrates the measured R , A , and T for different content of CNFs at 700 MHz. In Figure 5.13, it can be seen that R increases with the increase in CNFs content, i.e. higher reflected power due to the increase in electrical conductivity. On the contrary, A increases initially with increasing in CNFs content, but decreases when the CNFs content is higher than 1.0 vol%. For the specimen containing above 1.5 vol% CNFs, it is evident that R is more dominant than A . This means that when the EM wave reaches the specimen, the amount of power reflected is more significant than that absorbed by the specimen itself. It is hence reckoned that the main contributor for EMI SE of the specimen is from the reflection of EM wave.

Figure 5.13 Transmittance (T), reflectance (R) and absorbance (A) of EM radiation against the content of CNFs at 700 MHz.

Table 5.1 lists overall SE of the CNFRSF and CNF composites (without HCMs) at different frequencies. It can be seen that the SE of CNFRSF is higher than that of CNF composites. According to Schelkunoff theory [150], multiple-reflections is a negative contribution to the overall SE and can be ignored if the wave encounters substantial

absorption loss as it propagates back and forth within the shield. Normally, the multiple-reflections requires the presence of an interface area [107]. A shield with a large interface area is a composite material containing fillers which have large surface area. Comparing to CNF composite without HCMs, CNFRSF possesses a larger surface area, i.e. due to the presence of HCMs. This means that the multiple-reflections effect in CNFRSF is more significant than that in CNF composite without HCMs with the same volume fraction of CNFs. However, from Table 5.1, it can be seen that a higher SE is achieved in CNFRSF as compared to CNF composites with the same filler loading. This could be attributed to a closer network structure in CNFRSF. It is noted that, for CNFRSF, CNFs could not be well distributed in the matrix due to the presence of the HCMs, as the HCMs occupy large volume of the matrix and affect the even distribution of CNFs. Nonetheless, with increasing CNFs loading, CNFs can connect with one another more easily and an electrically conductive network was formed. As a result, comparing to CNF composite without HCMs, CNFRSF with the same CNFs volume fraction, has a relatively closer electric network. This led to higher SE. Herein, the network effect on SE is more significant to that contributed by multiple-reflections. In other words, the overall higher SE of CNFRSF than that of CNF composites is the sum of a relatively small decrease in SE that is due to the multiple-reflections effect and the increase in SE that is due to the closer CNFs network.

Table 5.2 compares the SE of CNFRSF and CNF composite as their phenolic resin matrix containing same volume fractions of CNFs. In this case, the conductive network of CNFs is the same in the CNFRSF and CNF composite. It is noted that the SE of CNFRSF is still higher than that of CNF composite. This means that the HCMs also have some contribution to the overall EMI SE. HCMs can connect one another by the network of the CNFs. Therefore, the bulk conductivity increases by the presence of conductive HCMs and leads to higher EMI SE.

Table 5.1 Comparison of SE of CNFRSF and CNF composite containing same volume fractions of CNFs.

Samples (CNFs volume fraction)	Frequency		
	400 MHz	700 MHz	1.2 GHz
CNFRSF (0.5 vol%)	2.30	1.40	5.22
CNF Composite (0.5 vol%)	1.86	1.16	3.27
CNFRSF (1.0 vol%)	5.40	5.27	11.34
CNF Composite (1.0 vol%)	3.22	2.63	6.35
CNFRSF (1.5 vol%)	10.37	9.93	16.38
CNF Composite (1.5 vol%)	6.26	5.87	10.71
CNFRSF (2.0 vol%)	20.79	19.53	24.88
CNF Composite (2.0 vol%)	12.14	10.76	17.06

Table 5.2 Comparison of SE of CNFRSF and CNF composite as the phenolic resin matrix containing same volume fractions of CNFs.

Samples (CNFs volume fraction)	Frequency		
	400 MHz	700 MHz	1.2 GHz
CNFRSF (0.5 vol%)	2.30	1.40	5.22
CNF Composite (0.7 vol%)	2.09	1.28	4.68
CNFRSF (1.0 vol%)	5.40	5.27	11.34
CNF Composite (1.4 vol%)	4.46	3.66	8.87
CNFRSF (1.5 vol%)	10.37	9.93	16.38
CNF Composite (2.1 vol%)	8.71	8.14	14.66
CNFRSF (2.0 vol%)	20.79	19.53	24.88
CNF Composite (2.8 vol%)	16.99	15.01	23.72

5.4 Concluding remarks

(1). Syntactic foam with CNFs reinforcement was prepared. The effects of CNFs content on mechanical and EMI SE properties of the syntactic foams were evaluated experimentally.

(2). Compressive strength of the syntactic foam remained almost constant with increasing CNFs content. This is because the microspheres in the CNFRSF are weaker and more brittle when the specimen is subjected to compressive loading.

(3). It was found that flexural strength and fracture toughness increased with increasing CNFs content and decreased beyond 1.5 vol% in CNFs content. The increasing trend indicated that the primary load bearing phases are CNF and the matrix instead of the microspheres when the specimen is subjected to flexural loading. On the other hand, the decreasing trend is attributed to the agglomeration and clustering of the CNFs.

(4). A step structure observed for syntactic foam containing low volume fraction in CNFs content is mainly due to the fracture of the matrix itself. With the addition of more CNFs, it is more difficult for the cracks to propagate along the matrix and this resulted in the improvement of fracture toughness.

(5) SE of the CNFRSF increases with increasing CNFs content. In addition, the syntactic foam having 2.0 vol% CNFs has a SE of 25 dB, which is good enough for most practical applications.

(6). Multiple-reflections provide a negative contribution to the overall shielding. This mechanism requires the presence of a large surface area or interface area in the shield. For the CNFRSF, the HCMs contributed both negatively and positively to the overall shielding effectiveness. The negative contribution is due to the large surface area within the shield. The positive contribution is ascribed to the achievement of a closer CNF network when HCMs were introduced into the polymer matrix. Compared to a relative minor decrease in SE due to multiple-reflections, a closer electrical network provide a

dramatic increase in SE, which leads that the SE of CNFRSF is superior to CNF composites without HCMs.

(7). The connectivity of HCMs can be improved by the CNFs network and leads to the improvement in the overall conductive network in the CNFRSF.

Chapter 6. Conclusions and future work

6.1 Conclusions

This thesis involves the study on the enhancement in mechanical properties and EMI shielding performance of syntactic foams. The ultimate goal of the work is to develop approaches for producing syntactic foams with better mechanical properties and/or higher EMI shielding performance, which will widen the application spectrum of the syntactic foams.

The work started from coupling agent approach. It was found that CA-HCMs could be achieved by the chemical reaction which involved oxidization of HCMs followed by the treatment with glutaric dialdehyde. It was found that compressive and flexural strengths decreased with increasing filler content and the maximum fracture toughness occurred at 28.1 vol% of filler content. The decreasing trend in compressive and flexural strengths is attributed to the increase in hollow space volume. The presence of the optimal fracture toughness indicates that the dominant toughening mechanism changed from the combination of crack deflection and bowing to the combination of crack bowing and debonding mechanisms beyond 28.1 vol% of filler content. It was also found that the mechanical properties of the syntactic foam containing CA-HCMs are better than those of the syntactic foam containing Un-HCMs, because coupling agent facilitated better adhesion between the HCMs and the matrix. Although the introduction of coupling agent could improve the mechanical properties of syntactic foams, it does not facilitate EMI shielding performance. The low volume fraction and low aspect ratio of HCMs result in no electrical network formation in the matrix, despite the fact that the introduction of coupling agent can improve the dispersion behavior of the filler. Only 1.7 dB of SE was obtained for the syntactic foam containing 28 vol% of filler, which is too

low for practical EMI shielding applications. In general, coupling agent approach improved mechanical properties without sacrificing the density. However, it had no effect on EMI SE. The foams developed with this approach can be used for fields which require higher mechanical properties and have little concern about EMI shielding performance. It is noted that, compared to traditional fillers, such as glass and ceramic microspheres, HCMs possess lower density. In this work, HCMs provide the lower density of resultant foam though they cannot form the electrical network.

In order to enhance the EMI shielding performance of syntactic foams, carbonization was attempted, considering the higher conducting of carbon matrix than polymer. Syntactic foam with carbon matrix could be achieved by thermal treatment of the syntactic foam containing HCMs with phenolic resin matrix. The process was followed by post-curing, pre-carbonization and carbonization. After carbonization, approximately 34% of the volume shrinkage and a 49% weight loss of composites occurred. It was found that the electrical conductivity of syntactic foam was increased by approximately seven orders of magnitude after carbonization and the resultant SE has improved by a factor of 16 compared to the syntactic foam before carbonization. This is attributed to the growth in sp^2 carbon structures in the matrix after carbonization which increases the formation of the interconnected electrical network. 30 dB of SE was obtained, which means that the material can shield over 99.91% of the incident EM radiation. It was found that reflection was the dominant mechanism due to the free electron in the carbon matrix. Multiple-reflections had a negative contribution to the overall SE at relatively low frequencies when the shield thickness is smaller than the skin depth. On the contrary, the effect of multiple-reflections can be ignored at high frequency. It was also found that the compressive and flexural strengths of syntactic foam are strongly dependent on heat-treatment temperature. The slight increase in compressive and flexure strengths after the post-curing was ascribed to the formation of long-chain, good

cross-linking polymeric structures in the matrix. After post-curing stage, the mechanical properties decreased, which is attributed to the introduction of more interval voids during carbonization. In general, the carbonization approach enhanced the EMI shielding performance with lower density though it decreased the mechanical properties. This approach can be applied in areas where high EMI shielding performance is critical and mechanical properties are not essential.

Attempts of inclusion of CNFs were aimed to simultaneously increase mechanical properties and EMI shielding performance of the syntactic foams. It was found that the compressive strength remained almost constant with increasing CNFs content because the phase of HCMs in CNFRSF is weaker and more brittle when the specimen is subjected to compressive loading. Flexural strength and fracture toughness was increased with increasing CNFs content, because the primary load bearing phase become CNFs and matrix itself instead of HCMs. A step structure was observed for the syntactic foam containing low volume fraction of CNFs, which corresponds to the failure of matrix itself. With the addition of more CNFs, the cracks propagation becomes more difficult along the matrix and hence results in the improvement of fracture toughness. When the content of CNFs was beyond 1.5 vol%, both the flexural strength and fracture toughness were decreased. This was ascribed to agglomeration and clustering of the CNFs. It was also found that the SE of CNFRSF increased with increase in CNFs content. SE of 25 dB was achievable in the sample with 2.0 vol% CNFs content, which means that the materials can shield 99.67% of incident EM wave and thus is good enough for most practical applications. Similarly, reflection is dominant instead of absorption. The SE performance of the CNFRSF was superior to the composites having either CNFs or HCMs only. The presence of HCMs provided the negative contribution to the overall shielding which resulted from the large surface area within the shield, and the positive contribution which derive from a formation of closer electrical network structure. It is also noted that the

addition of CNFs leads to the slight increase in density. The CNFs reinforcement approach led to foams with simultaneously high mechanical properties and good EMI shielding performance, which will widen the application spectrum of the syntactic foams.

6.2 Future work

The results of the present work have inspired the following interesting future work:

(1). Effect of coupling agent on CNFRSF

In Chapter 3, the results showed that the addition of coupling agent can facilitate better adhesion between HCMs and phenolic resin matrix. In Chapter 5, CNFRSF was developed. It is noted that dispersion of CNF plays a key role in improving the properties of syntactic foam. Surface modification is reckoned to be an effective way to improve the dispersion of CNF in the matrix. This could be facilitated by the use of coupling agent, which is expected to induce a change in the surface properties of CNFs. Figure 6.1 illustrates the interfacial reaction among the oxidized HCM, the oxidized CNF, and the phenolic resin, in the presence of glutaric dialdehyde. It is expected that the mechanical properties will be further improved with the interfacial modification between CNFs and phenolic resin matrix. Besides the mechanical properties, the electrical conductivity is expected to be increased as well due to the better formation of the electrical network, resulting in the higher EMI SE.

Figure 6.1 Schematic process of chemical reaction among the oxidized HCM, the oxidized CNF and coupling agent of glutaric dialdehyde.

(2). Metal-coating HCMs

The EMI shielding performance of syntactic foams is limited by their poor electrical conductivity of its traditional filler. To enable wider applications for syntactic foam, it is necessary to increase the conductivity of the filler. In the previous work, a novel HCM has been successfully produced. However, since its high electrical resistivity, a desirable EMI SE value was still not achieved which results from the poor intrinsic conductivity of HCMs. This problem could be solved by applying a thin layer of metal on the surface of HCMs. Copper and nickel are the two main metals used as coating

materials. Electroless plating [151-159] is a typical techniques used in metal coatings. In general, it involves the metal deposition onto catalytic surface without an external electric current source. However, it has not been used for syntactic foams. Thus, the investigation in EMI shielding performance of syntactic foam containing metal-coated HCMs will be interesting. Figure 6.2 illustrates the proposed images of syntactic foams containing metal-coated HCMs.

Figure 6.2 Schematic of proposed preparation process of syntactic foam containing copper coated HCMs (a) and nickel coated HCMs (b), respectively.

Reference

- [1] Charles Sturt University.
- [2] Mazumdar S. K. (2001). Introduction. Composites Manufacturing: Materials, Product, and Process Engineering. Boca Raton London New York Washington, CRC Press.
- [3] Gladysz G. M. , Perry B. , McEachen G. & Lula J. (2006). Three-phase syntactic foams: structure-property relationships *Journal of Materials Science* 41, 4085-4092.
- [4] Karst G. (2002). Novel processing of high-performance structural syntactic foams.
- [5] Rahaman M. , Chaki T. K. & Khastgir D. (2011). Development of high performance EMI shielding material from EVA, NBR, and their blends: effect of carbon black structure *Journal of Materials Science* 46, 3989-3999.
- [6] Sohi N. J. S. , Rahaman M. & Khastgir D. (2011). Dielectric Property and Electromagnetic Interference Shielding Effectiveness of Ethylene Vinyl Acetate-Based Conductive Composites: Effect of Different Type of Carbon Fillers *Polymer Composites* 32, 1148-1154.
- [7] Das N. C. , Chaki T. K. , Khastgir D. & Chakraborty A. (2001). Electromagnetic interference shielding effectiveness of ethylene vinyl acetate based conductive composites containing carbon fillers *Journal of Applied Polymer Science* 80, 1601-1608.
- [8] Morgan D., Ed. (1995). *A handbook of EMC testing and measurement*. Signal Processing. London, United Kingdom, Peter Peregrinus Ltd. on behalf of the Institution of Electrical Engineers (IEE).

-
- [9] Wouterson E. M. , Boey F. Y. C. , Hu X. & Wong S. C. (2007). Effect of fiber reinforcement on the tensile, fracture and thermal properties of syntactic foam *Polymer* 48, 3183-3191.
- [10] Alonso M. V. , Auad M. L. & Nutt S. (2006). Short-fiber-reinforced epoxy foams *Composites Part a-Applied Science and Manufacturing* 37, 1952-1960.
- [11] Choi M. H. , eon B. H. & Chung I. J. (2000). The effect of coupling agent on electrical and mechanical properties of carbon fiber/phenolic resin composites *Polymer* 41, 3243-3252.
- [12] Liu X. , Xia Q. M. , Gao J. T. , Zhang Q. H. & Icafp (2009). Dispersion of carbon black and electrical conductive properties of CB/PBT composites.
- [13] Palumbo M. , Donzella G. , Tempesti E. & Ferruti P. (1996). On the compressive elasticity of epoxy resins filled with hollow glass microspheres *Journal of Applied Polymer Science* 60, 47-53.
- [14] Palumbo M. & Tempesti E. (1998). On the nodular morphology and mechanical behavior of a syntactic foam cured in thermal and microwave fields *Acta Polymerica* 49, 482-486.
- [15] Gupta N. , Kishore , Woldeesenbet E. & Sankaran S. (2001). Studies on compressive failure features in syntactic foam material *Journal of Materials Science* 36, 4485-4491.
- [16] Gupta N. , Woldeesenbet E. & Kishore (2002). Compressive fracture features of syntactic foams-microscopic examination *Journal of Materials Science* 37, 3199-3209.
- [17] Gupta N. , Woldeesenbet E. , Kishore & Sankaran S. (2002). Response of syntactic foam core sandwich structured composites to three-point bending *Journal of Sandwich Structures & Materials* 4, 249-272.

-
- [18] Islam M. M. & Kim H. S. (2007). Novel syntactic foams made of ceramic hollow micro-spheres and starch: theory, structure and properties *Journal of Materials Science* 42, 6123-6132.
- [19] Song B. & Chen W. (2004). Dynamic compressive response and failure behavior of an epoxy syntactic foam *Journal of Composite Materials* 38, 915-936.
- [20] Song B. , Chen W. N. , Yanagita T. & Frew D. J. (2005). Confinement effects on the dynamic compressive properties of an epoxy syntactic foam *Composite Structures* 67, 279-287.
- [21] Song B. , Chen W. N. , Yanagita T. & Frew D. J. (2005). Temperature effects on dynamic compressive behavior of an epoxy syntactic foam *Composite Structures* 67, 289-298.
- [22] Erikson R. (1999). Mechanical Engineering Magazine.
- [23] Gupta N. , Karthikeyan C. S. , Sankaran S. & Kishore (1999). Correlation of processing methodology to the physical and mechanical properties of syntactic foams with and without fibers *Materials Characterization* 43, 271-277.
- [24] John B. & Nair C. P. R., Eds. (2010). *Update on Syntactic Foams*. Shawbury, Shrewsbury, Shropshire, SY4 4NR, United Kingdom, iSmithers – A Smithers Group Company.
- [25] Lin Y. G. , Sautereau H. & Pascault J. P. (1986). BDMA-catalyzed DDA-epoxy resin system- temperature and composition effects on curing mechanism *Journal of Polymer Science Part a-Polymer Chemistry* 24, 2171-2184.
- [26] Li Y. S. , Li M. S. & Chang F. C. (1999). Kinetics and curing mechanism of epoxy and boron trifluoride monoethyl amine complex system *Journal of Polymer Science Part a-Polymer Chemistry* 37, 3614-3624.
- [27] Barral L. , Cano J. , Lopez J. , Lopez-Bueno I. , Noguiera P. , Abad M. J., et al. (2000). Kinetic studies of the effect of ABS on the curing of an

- epoxy/cycloaliphatic amine resin *Journal of Polymer Science Part B-Polymer Physics* 38, 351-361.
- [28] Barral L. , Cano J. , Lopez J. , Lopez-Bueno I. , Nogueira P. , Abad M. J., et al. (2000). Blends of an epoxy/cycloaliphatic amine resin with poly(ether imide) *Polymer* 41, 2657-2666.
- [29] Serier A. , Pascault J. P. & My L. T. (1991). Reactions in aminosilane epoxy prepolymer systems. 1. kinetics of epoxy amine reactions *Journal of Polymer Science Part a-Polymer Chemistry* 29, 209-218.
- [30] Chen W. Y. , Wang Y. Z. & Chang F. C. (2004). Study on curing kinetics and curing mechanism of epoxy resin based on diglycidyl ether of bisphenol A and melamine phosphate *Journal of Applied Polymer Science* 92, 892-900.
- [31] Hara O. (1990) Curing Agents for Epoxy Resin.
- [32] John B. , Nair C. P. R. & Ninan K. N. (2010). Effect of nanoclay on the mechanical, dynamic mechanical and thermal properties of cyanate ester syntactic foams *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing* 527, 5435-5443.
- [33] Zhang X. Q. & Solomon D. H. (1998). The chemistry of novolac resins .6. Reactions between benzoxazine intermediates and model phenols *Polymer* 39, 405-412.
- [34] Zhang X. Q. , Potter A. C. & Solomon D. H. (1998). The chemistry of novolac resins .5. Reactions of benzoxazine intermediates *Polymer* 39, 399-404.
- [35] Zhang X. Q. , Potter A. C. & Solomon D. H. (1998). The chemistry of novolac resins: Part 8. Reactions of para-hydroxybenzylamines with model phenols *Polymer* 39, 1967-1975.

-
- [36] Zhang X. Q. , Potter A. C. & Solomon D. H. (1998). The chemistry of novolac resins: Part 7. Reactions of para-hydroxybenzylamine intermediates *Polymer* 39, 1957-1966.
- [37] Zhang X. Q. , Looney M. G. , Solomon D. H. & Whittaker A. K. (1997). The chemistry of novolac resins .3. C-13 and N-15 nmr studies of curing with hexamethylenetetramine *Polymer* 38, 5835-5848.
- [38] Dominguez J. C. , Alonso M. V. , Olier M. , Rojo E. & Rodriguez F. (2010). Kinetic study of a phenolic-novolac resin curing process by rheological and DSC analysis *Thermochimica Acta* 498, 39-44.
- [39] Rodia J. S. (1967). Role of para-substituted phenolic in curing resole-type phenolic resins *Journal of Polymer Science Part a-1-Polymer Chemistry* 5, 2807.
- [40] Katovic Z. (1967). Kinetics of formation of dibenzyl ether linkage during curing of resole-type phenol-formaldehyde resin by DTA and infrared spectroscopy *Journal of Applied Polymer Science* 11, 95.
- [41] Katovic Z. (1967). Curing of resole-type phenol-formaldehyde resin *Journal of Applied Polymer Science* 11, 85.
- [42] So S. & Rudin A. (1990). Effects of resin and curing parameters on the degree of cure of resole phenolic resins and woodflour composites *Journal of Applied Polymer Science* 40, 2135-2149.
- [43] Focke W. W. , Smit M. S. , Tolmay A. T. , Vanderwalt L. S. & Vanwyk W. L. (1991). Differential scanning calorimetry analysis of thermoset cure kinetics-phenolic resole resin *Polymer Engineering and Science* 31, 1665-1669.
- [44] Zhou D. P. , Du S. P. , Yu L. Q. & Liu Z. (2011). Nonisothermal Curing of a Solid Resole Phenolic Resin *Journal of Applied Polymer Science* 121, 1938-1945.
- [45] Balch D. K. & Dunand D. C. (2006). Load partitioning in aluminum syntactic foams containing ceramic microspheres *Acta Materialia* 54, 1501-1511.

-
- [46] Ribeiro J. , Plaksin I. , Campos J. , Mendes R. & Gois J. (2000). Process of shock attenuation inside a hollow glass microsphere/polymeric composite media. Shock Compression of Condensed Matter-1999, Pts 1 and 2. Furnish M. D., Chhabildas L. C., Hixson R. S. 505: 559-562.
- [47] Yung K. C. , Zhu B. L. , Yue T. M. & Xie C. S. (2009). Preparation and properties of hollow glass microsphere-filled epoxy-matrix composites *Composites Science and Technology* 69, 260-264.
- [48] Balch D. K. & Dunand D. C. (2002). Mechanical properties and in-situ diffraction strain measurements in aluminum - Mullite microsphere syntactic foams produced by liquid metal infiltration. Processing and Properties of Lightweight Cellular Metals and Structures. Ghosh A., Sanders T. H., Claar T. D.: 251-260.
- [49] Wouterson E. M. , Boey F. Y. C. , Hu X. & Wong S. C. (2004). Fracture and impact toughness of syntactic foam *Journal of Cellular Plastics* 40, 145-154.
- [50] Rizzi E. , Papa E. & Corigliano A. (2000). Mechanical behavior of a syntactic foam: experiments and modeling *International Journal of Solids and Structures* 37, 5773-5794.
- [51] Phlegm H. K. (2009). *The role of the chemist in automotive design / H.K. Phlegm*, Boca Raton, FL : CRC Press/Taylor & Francis, c2009.
- [52] Wouterson E. M. , Boey F. Y. C. , Hu X. & Wong S. C. (2005). Specific properties and fracture toughness of syntactic foam: Effect of foam microstructures *Composites Science and Technology* 65, 1840-1850.
- [53] Hollow glass microspheres, 3M.
- [54] Narkis M. , Gerchovich M. , Puterman M. & Kenig S. (1982). Syntactic foams - 3. Three-phase materials produced from resin coated microballoons *Journal of Cellular Plastics* 18, 230-232.

-
- [55] Samsudin S. S. , Ariff Z. M. , Zakaria Z. & Bakar A. A. (2011). Development and characterization of epoxy syntactic foam filled with epoxy hollow spheres *Express Polymer Letters* 5, 653-660.
- [56] Klempner D. , Sendijarevic V. & Aseeva R. M. (2004). *Handbook of polymeric foams and foam technology*, Munich : Hanser Publishers ; Cincinnati : Hanser Gardener [i.e. Gardner] Publications, c2004. 2nd ed. / edited by Daniel Klempner and Vahid Sendijarevic ; with contributions by R.M. Aseeva ... [et al.].
- [57] Rutz B. H. & Berg J. C. (2010). A review of the feasibility of lightening structural polymeric composites with voids without compromising mechanical properties *Advances in Colloid and Interface Science* 160, 56-75.
- [58] Hollow phenolic microspheres, Eastech Chemical, INC.
- [59] Tomonaga A., inventor Electromagnetic wave absorbing material containing carbon microspheres patent 3951904. 1976.
- [60] S.Y.Chew , Bo Z. & Boey F. Y. C. Analysis of hollow phenolic and carbon microspheres; 1999.
- [61] Ding J. Y. & Day D. E. (1991). Preparation of silica glass microspheres by sol-gel processing *Journal of Materials Research* 6, 168-174.
- [62] Qiu L. H. , Fu Y. B. , Tang Y. J. , Wei Y. , Zheng Y. M. , Shi T., et al. (2002). Hollow glass microsphere production for laser direct-driven fusion targets on Shen Guang II *Science in China Series a-Mathematics Physics Astronomy* 45, 371-377.
- [63] Sokol E. V. , Maksimova N. V. , Volkova N. I. , Nigmatulina E. N. & Frenkel A. E. (2000). Hollow silicate microspheres from fly ashes of the Chelyabinsk brown coals *Fuel Processing Technology* 67, 35-52.
- [64] Bica I. (2000). Formation of glass microspheres with rotating electrical arc *Materials Science and Engineering B-Solid State Materials for Advanced Technology* 77, 210-212.

-
- [65] Schumacher R. F., inventor Savannah River Nuclear Solutions LLC, assignee. Apparatus and process to enhance the uniform formation of hollow glass. 2010.
- [66] Liu X. Z. , Li H. J. , Ma T. M. & Li K. Z. (2009). Preparation of phenolic hollow microspheres via in situ polymerization *Polymer International* 58, 465-468.
- [67] Klempner D. & Frisch K. C. (1991). *Handbook of polymeric foams and foam technology*, Munich ; New York : Hanser ; New York : Distributed in U.S.A. and Canada by Oxford University Press, c1991.
- [68] Tamai H. , Sumi T. & Yasuda H. (1996). Preparation and characteristics of fine hollow carbon particles *Journal of Colloid and Interface Science* 177, 325-325.
- [69] Klempner D. & Frisch K. C. (1991). *Handbook of polymeric foams and foam technology / edited by Daniel Klempner and Kurt C. Frisch*, Munich ; New York : Hanser ; New York : Distributed in U.S.A. and Canada by Oxford University Press, c1991.
- [70] Puterman M. , Narkis M. & Kenig S. (1980). Syntactic foams 1. preparation, structure and properties *Journal of Cellular Plastics* 16, 223-229.
- [71] M. M. A., inventor E. I. Du Pont de Nemours and Company assignee. Impact resistant thermoplastic syntactic foam composite and method. 1994.
- [72] S D. P. P. , E F. J. , E R. R. & Alois W., inventors; Hughes Aircraft Company assignee. Fiber-reinforced syntactic foam composites and method of forming same. 1986.
- [73] S H. E. , J B. D. & L M. J., inventors; McDonnell Douglas, assignee. Thermosetting syntactic foams and their preparation. 2000.
- [74] Cravens T. E. (1973). Syntactic foams utilizing saran microspheres *Journal of Cellular Plastics* 9, 260-267.
- [75] Mudge R. S., inventor The Boeing Company, assignee. Process for making a low density syntactic foam product and the resultant product. 1988.

-
- [76] Lin B. , Sundararaj U. & Potschke P. (2006). Melt mixing of polycarbonate with multi-walled carbon nanotubes in miniature mixers *Macromolecular Materials and Engineering* 291, 227-238.
- [77] Lee S. M. (1993). *Handbook of composite reinforcements*, New York : VCH, c1993.
- [78] Gupta N. , Ye R. & Porfiri M. Comparison of tensile and compressive characteristics of vinyl ester/glass microballoon syntactic foams *Composites Part B: Engineering* 41, 236-245.
- [79] Lei S. , Guo Q. , Shi J. & Liu L. Preparation of phenolic-based carbon foam with controllable pore structure and high compressive strength *Carbon* In Press, Accepted Manuscript.
- [80] Gupta N. & Woldeesenbet E. (2003). Hygrothermal studies on syntactic foams and compressive strength determination *Composite Structures* 61, 311-320.
- [81] Gupta N. , Woldeesenbet E. & Mensah P. (2004). Compression properties of syntactic foams: effect of cenosphere radius ratio and specimen aspect ratio *Composites Part A: Applied Science and Manufacturing* 35, 103-111.
- [82] Song B. , Chen W. , Yanagita T. & Frew D. J. (2005). Confinement effects on the dynamic compressive properties of an epoxy syntactic foam *Composite Structures* 67, 279-287.
- [83] Viot P. , Shankar K. & Bernard D. (2008). Effect of strain rate and density on dynamic behaviour of syntactic foam *Composite Structures* 86, 314-327.
- [84] Li P. , Petrinic N. , Siviour C. R. , Froud R. & Reed J. M. (2009). Strain rate dependent compressive properties of glass microballoon epoxy syntactic foams *Materials Science and Engineering: A* 515, 19-25.
- [85] Tao X. F. & Zhao Y. Y. (2009). Compressive behavior of Al matrix syntactic foams toughened with Al particles *Scripta Materialia* 61, 461-464.

- [86] Gupta N. , Kishore & Sankaran S. (1999). On the characterisation of syntactic foam core sandwich composites for compressive properties *Journal of Reinforced Plastics and Composites* 18, 1347-1357.
- [87] Lin W. H. & Jen M. H. R. (1998). Manufacturing and mechanical properties of glass bubbles epoxy particulate composite *Journal of Composite Materials* 32, 1356-1390.
- [88] Li P. , Petrinic N. , Siviour C. R. , Froud R. & Reed J. M. (2009). Strain rate dependent compressive properties of glass microballoon epoxy syntactic foams *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing* 515, 19-25.
- [89] Gupta N. & Woldesenbet E. (2005). Characterization of flexural properties of syntactic foam core sandwich composites and effect of density variation *Journal of Composite Materials* 39, 2197-2212.
- [90] Kishore , Shankar R. & Sankaran S. (2005). Short beam three point bend tests in syntactic foams. Part 1: Microscopic characterization of the failure zones *Journal of Applied Polymer Science* 98, 673-679.
- [91] Kishore , Shankar R. & Sankaran S. (2005). Short-beam three-point bend tests in syntactic foams. Part II: Effect of microballoons content on shear strength *Journal of Applied Polymer Science* 98, 680-686.
- [92] Kishore , Shankar R. & Sankaran S. (2005). Short-beam three-point bend test study in syntactic foam. Part III: Effects of interface modification on strength and fractographic features *Journal of Applied Polymer Science* 98, 687-693.
- [93] Tagliavia G. , Porfiri M. & Gupta N. (2010). Analysis of flexural properties of hollow-particle filled composites *Composites Part B-Engineering* 41, 86-93.
- [94] Rotheron R. N. (1995). *Particulate-filled polymer composites* / R.N. Rotheron, New York : Longman Scientific and Technical, 1995.

-
- [95] Lee J. & Yee A. F. (2000). Fracture of glass bead/epoxy composites: on micro-mechanical deformations *Polymer* 41, 8363-8373.
- [96] Wouterson E. M. , Boey F. Y. C. , Hu X. & Wong S.-C. (2005). Specific properties and fracture toughness of syntactic foam: Effect of foam microstructures *Composites Science and Technology* 65, 1840-1850.
- [97] Kishore , Shankar R. & Sankaran S. (2006). Effects of microballoons' size and content in epoxy on compressive strength and modulus *Journal of Materials Science* 41, 7459-7465.
- [98] Kawaguchi T. & Pearson R. A. (2003). The effect of particle–matrix adhesion on the mechanical behavior of glass filled epoxies. Part 2. A study on fracture toughness *Polymer* 44, 4239-4247.
- [99] Plueddemann E. P. (1991). *Silane coupling agents* / Edwin P. Plueddemann, New York : Plenum Press, c1991.2nd ed.
- [100] Koopman M. , Chawla K. K. , Carlisle K. B. & Gladysz G. M. (2006). Microstructural failure modes in three-phase glass syntactic foams *Journal of Materials Science* 41, 4009-4014.
- [101] Karthikeyan C. S. , Sankaran S. & Kishore (2000). Influence of chopped strand fibres on the flexural behaviour of a syntactic foam core system *Polymer International* 49, 158-162.
- [102] John B. , Nair C. P. R. & Ninan K. N. (2008). Tensile and Flexural Properties of Glass-fibre-reinforced Cyanate Ester Syntactic Foams *Polymers & Polymer Composites* 16, 431-438.
- [103] Wouterson E. m. Toughening of low-weight foam-based composites for defense applications. Nanyang technological university, Degree of doctor of philosophy, 2007.

-
- [104] Karthikeyan C. S. , Sankaran S. , Kumar M. N. J. & Kishore (2001). Processing and compressive strengths of syntactic foams with and without fibrous reinforcements *Journal of Applied Polymer Science* 81, 405-411.
- [105] Yang Y. L. & Gupta M. C. (2005). Novel carbon nanotube-polystyrene foam composites for electromagnetic interference shielding *Nano Letters* 5, 2131-2134.
- [106] Huang J. C. (1995). EMI Shielding Plastics A Review *Advances in Polymer Technology* 14, 137-150.
- [107] Chung D. D. L. (2001). Electromagnetic interference shielding effectiveness of carbon materials *Carbon* 39, 279-285.
- [108] Al-Saleh M. H. & Sundararaj U. (2009). Electromagnetic interference shielding mechanisms of CNT/polymer composites *Carbon* 47, 1738-1746.
- [109] Geetha S. , Kumar K. K. S. , Rao C. R. K. , Vijayan M. & Trivedi D. C. (2009). EMI Shielding: Methods and Materials-A Review *Journal of Applied Polymer Science* 112, 2073-2086
- [110] A.Sihvola, Ed. (1999). *Electromagnetic mixing formulas and application*. London, United Kingdom, The insituition of Electrical Engineers.
- [111] Koledintseva M. , Ravva P. C. , DuBroff R. , Drewniak J. , Rozanov K. & Archambeault B. (2005). Engineering of composite media for shields at microwave frequencies. 2005 International Symposium on Electromagnetic Compatibility, EMC 2005, August 8, 2005 - August 12, 2005, Chicago, IL, United states, Institute of Electrical and Electronics Engineers Inc.
- [112] Li N. , Huang Y. , Du F. , He X. B. , Lin X. , Gao H. J., et al. (2006). Electromagnetic interference (EMI) shielding of single-walled carbon nanotube epoxy composites *Nano Letters* 6, 1141-1145.
- [113] Das N. C. , Khastgir D. , Chaki T. K. & Chakraborty A. (2000). Electromagnetic interference shielding effectiveness of carbon black and carbon fibre filled EVA

- and NR based composites *Composites Part a-Applied Science and Manufacturing* 31, 1069-1081.
- [114] Al-Saleh M. H. & Sundararaj U. (2008). Electromagnetic interference (EMI) shielding effectiveness of PP/PS polymer blends containing high structure carbon black *Macromolecular Materials and Engineering* 293, 621-630.
- [115] Jana P. B. , Mallick A. K. & De S. K. (1992). Effects of sample thickness and fiber aspect ratio on EMI shielding effectiveness of carbon-fiber filled polychloroprene composites in the X-band frequency range *Ieee Transactions on Electromagnetic Compatibility* 34, 478-481.
- [116] Wen-Yen C. & Kai-Yuan C. (1997). Processing conditions for electromagnetic interference shielding effectiveness and mechanical properties of acrylonitrile-butadiene-styrene based composites *Polymer Composites* 18, 748-756.
- [117] Krueger Q. J. & King J. A. (2003). Synergistic effects of carbon fillers on shielding effectiveness in conductive nylon 6,6-and polycarbonate-based resins *Advances in Polymer Technology* 22, 96-111.
- [118] Luo X. C. & Chung D. D. L. (1999). Electromagnetic interference shielding using continuous carbon-fiber carbon-matrix and polymer-matrix composites *Composites Part B-Engineering* 30, 227-231.
- [119] Chou K. S. , Huang K. C. & Shih Z. H. (2005). Effect of mixing process on electromagnetic interference shielding effectiveness of nickel/acrylonitrile-butadiene-styrene composites *Journal of Applied Polymer Science* 97, 128-135.
- [120] Chen S. C. , Chien R. D. , Lee P. H. & Huang J. S. (2005). Effects of molding conditions on the electromagnetic interference performance of conductive ABS parts *Journal of Applied Polymer Science* 98, 1072-1080.

-
- [121] Bagwell R. M. , McManaman J. M. & Wetherhold R. C. (2006). Short shaped copper fibers in an epoxy matrix: Their role in a multifunctional composite *Composites Science and Technology* 66, 522-530.
- [122] Chiang W. Y. & Chiang Y. S. (1992). Effect of titanate coupling agent on electromagnetic interference shielding effectiveness and mechanical properties of PC- ABS-NCF composite *Journal of Applied Polymer Science* 46, 673-681.
- [123] Im J. S. , Kim J. G. & Lee Y. S. (2009). Fluorination effects of carbon black additives for electrical properties and EMI shielding efficiency by improved dispersion and adhesion *Carbon* 47, 2640-2647.
- [124] Li Q. F. , Xu Y. H. , Yoon J. S. & Chen G. X. (2011). Dispersions of carbon nanotubes/polyhedral oligomeric silsesquioxanes hybrids in polymer: the mechanical, electrical and EMI shielding properties *Journal of Materials Science* 46, 2324-2330.
- [125] Wen S. & Chung D. D. L. (2005). Pitch-matrix composites for electrical, electromagnetic and strain-sensing applications *Journal of Materials Science* 40, 3897-3903.
- [126] Liu Q. L. , Zhang D. , Fan T. X. , Gu J. J. , Miyamoto Y. & Chen Z. X. (2008). Amorphous carbon-matrix composites with interconnected carbon nano-ribbon networks for electromagnetic interference shielding *Carbon* 46, 461-465.
- [127] Lee B. O. , Woo W. J. , Park H. S. , Hahm H. S. , Wu J. P. & Kim M. S. (2002). Influence of aspect ratio and skin effect on EMI shielding of coating materials fabricated with carbon nanofiber/PVDF *Journal of Materials Science* 37, 1839-1843.
- [128] Yang S. Y. , Lozano K. , Lomeli A. , Foltz H. D. & Jones R. (2005). Electromagnetic interference shielding effectiveness of carbon nanofiber/LCP composites *Composites Part a-Applied Science and Manufacturing* 36, 691-697.

-
- [129] Lee B. O. , Woo W. J. & Kim M. S. (2001). EMI shielding effectiveness of carbon nanofiber filled poly(vinyl alcohol) coating materials *Macromolecular Materials and Engineering* 286, 114-118.
- [130] Zhang C. S. , Ni Q. Q. , Fu S. Y. & Kurashiki K. (2007). Electromagnetic interference shielding effect of nanocomposites with carbon nanotube and shape memory polymer *Composites Science and Technology* 67, 2973-2980.
- [131] Al-Saleh M. H. & Sundararaj U. (2009). A review of vapor grown carbon nanofiber/polymer conductive composites *Carbon* 47, 2-22.
- [132] Gulyas J. , Rosenberger S. , Foldes E. & Pukanszky B. (2000). Chemical modification and adhesion in carbon fiber/epoxy micro-composites; Coupling and surface coverage *Polymer Composites* 21, 387-395.
- [133] Kaynak C. , Orgun O. & Tincer T. (2005). Matrix and interface modification of short carbon fiber-reinforced epoxy *Polymer Testing* 24, 455-462.
- [134] Hertzberg R. W. (1995). *Deformation and Fracture Mechanics of Engineering Materials*. New York, Wiley.
- [135] Wilson P. F. , Ma M. T. & Adams J. W. (1988). Techniques for measuring the electromagnetic shielding effectiveness of materials. 1. Far-field source simulation *IEEE T Electromagn C* 30, 239-250.
- [136] Badic M. , Marinescu M. J. & Ieee I. (2000). On the complete theory of coaxial TEM cells. 2000 Ieee International Symposium on Electromagnetic Compatibility, Vols 1 and 2, Symposium Record: 897-902.
- [137] Celozzi S. , Araneo R. & Lovat G. (2008). *Shielding Effectiveness of Stratified Media. Electromagnetic Shielding*, John Wiley & Sons, Inc.
- [138] Bunn P. & Mottram J. T. (1993). Manufacture and compression properties of syntactic foams *Composites* 24, 565-571.

- [139] Fine T. , Sautereau H. & Sauvant-Moynot V. (2003). Innovative processing and mechanical properties of high temperature syntactic foams based on a thermoplastic/thermoset matrix *Journal of Materials Science* 38, 2709-2716.
- [140] Luxmoore AR O. D., Ed. (1980). *The mechanics of syntactic foams*. Barking, Applied Science Publishers.
- [141] Kawaguchi T. & Pearson R. A. (2003). The effect of particle-matrix adhesion on the mechanical behavior of glass filled epoxies. Part 2. A study on fracture toughness *Polymer* 44, 4239-4247.
- [142] Joseph Chapman Anderson , K. D. Leavers , P. Leever & Rawlings R. D. (2003). *Materials science for engineers*, CRC Press.
- [143] Kuan C. F. , Kuan H. C. , Ma C. C. M. , Wu H. L. & Chen C. Y. (2006). Study on the polydimethylsiloxane polyurethane modified novolac type epoxy precursor for manufacturing carbon-carbon composites *Journal of Composite Materials* 40, 717-731.
- [144] Tse-Hao Ko W.-S. K. Y.-R. L. (2000). The influence of post-cure on properties of carbon/phenolic resin cured composites and their final carbon/carbon composites *Polymer Composites* 21, 96-103.
- [145] Trick K. A. & Saliba T. E. (1995). Mechanisms of the pyrolysis of phenolic resin in a carbon/phenolic composite *Carbon* 33, 1509-1515.
- [146] Chhowalla M. , Robertson J. , Chen C. W. , Silva S. R. P. , Davis C. A. ,Amaratunga G. A. J., et al. (1997). Influence of ion energy and substrate temperature on the optical and electronic properties of tetrahedral amorphous carbon (ta-C) films *Journal of Applied Physics* 81, 139-145.
- [147] Shui X. P. & Chung D. D. L. (1997). Nickel filament polymer-matrix composites with low surface impedance and high electromagnetic interference shielding effectiveness *Journal of Electronic Materials* 26, 928-934.

-
- [148] Perez R., Ed. (1995). Handbook of Electromagnetic Compatibility.
- [149] Lundgren U. , Ekman J. & Delsing J. (2006). Shielding effectiveness data on commercial thermoplastic materials *IEEE T Electromagn C* 48, 766-773.
- [150] Gonschorek K.-H. & Vick R. (2009). Skin Effect and Shielding Theory of Schelkunoff Electromagnetic Compatibility for Device Design and System Integration, Springer Berlin Heidelberg.
- [151] Tzeng S. S. & Chang F. Y. (2001). EMI shielding effectiveness of metal-coated carbon fiber-reinforced ABS composites *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing* 302, 258-267.
- [152] Huang C. Y. & Mo W. W. (2002). The effect of attached fragments on dense layer of electroless Ni/P deposition on the electromagnetic interference shielding effectiveness of carbon fibre/acrylonitrile-butadiene-styrene composites *Surface & Coatings Technology* 154, 55-62.
- [153] Park S. J. , Jang Y. S. & Rhee K. Y. (2002). Interlaminar and ductile characteristics of carbon fibers-reinforced plastics produced by nanoscaled electroless nickel plating on carbon fiber surfaces *Journal of Colloid and Interface Science* 245, 383-390.
- [154] Huang C. Y. , Mo W. W. & Roan M. L. (2004). Studies on the influence of double-layer electroless metal deposition on the electromagnetic interference shielding effectiveness of carbon fiber/ABS composites *Surface & Coatings Technology* 184, 163-169.
- [155] Gao H. Q. , Wang L. D. & Fei W. D. (2007). Electroless plating copper coating of Al18B4O33 whisker for interface improvement of whisker reinforced aluminium matrix composite *Materials Science and Technology* 23, 1497-1504.

-
- [156] Zhang H. J. & Liu Y. (2008). Preparation and microwave properties of Ni hollow fiber by electroless plating-template method *Journal of Alloys and Compounds* 458, 588-594.
- [157] Byeon J. H. & Kim J. W. (2010). Novel electroless copper deposition on carbon fibers with environmentally friendly processes *Journal of Colloid and Interface Science* 348, 649-653.
- [158] Hamid Z. A. & Aal A. A. (2010). Effect of electroless process parameters for nickel-phosphorous coatings on carbon fibres *Anti-Corrosion Methods and Materials* 57, 173-179.
- [159] Park K. Y. , Han J. H. , Lee S. B. & Yi J. W. (2011). Microwave absorbing hybrid composites containing Ni-Fe coated carbon nanofibers prepared by electroless plating *Composites Part a-Applied Science and Manufacturing* 42, 573-578.

Publication List

1. **Liying Zhang**, J. Ma (2013). Effect of carbon nanofiber reinforcement on mechanical properties of syntactic foam *Materials Science & Engineering A*, Volume 547, Issue 1, Pages 191-196.
2. **Liying Zhang**, J. Ma (2010). Effect of coupling agent on mechanical properties of hollow carbon microsphere / phenolic resin syntactic foam *Composites Science and Technology*, Volume 70, Issue 8, Pages 1265-1271.
3. **Liying Zhang**, J. Ma (2009). Processing and characterization of syntactic carbon foams containing hollow carbon microspheres *Carbon*, Volume 47, Issue 6, Pages 1451-1456.
4. **Liying Zhang**, L.B.Wang, Kye-Yak See, J. Ma (2013). Effect of carbon nanofiber reinforcement on electromagnetic interference shielding effectiveness of syntactic foam *Journal of materials science* under review.